THREE WAY CONVERSION CATALYSTS FOR AUTOMOTIVE POLLUTION ABATEMENT

Patrick L. Burk*, Zhicheng Hu, Harold N. Rabinowitz, and Samuel J. Tauster, Shau-Lin F. Chen
Engelhard Corporation, 101 Wood Ave., Iselin, New Jersey 08830

Keywords: Three Way Conversion Catalysts, Palladium, Sulfur

INTRODUCTION

The revisions to the Clean Air Act of 1990 and recent regulatory actions taken by the California Air Resources Board mandate the development of automobiles with much lower tailpipe emissions. For the original equipment manufacturers (OEM's) to meet the target fleet emissions numbers for automobiles defined in California's Low Emission Vehicle program, the OEM's must qualify each model into one of the emissions categories defined in Table 1. The emissions are calculated using the Federal Test Procedure (FTP) protocol wherein a test vehicle fitted with a catalytic converter is driven on a chassis rolls over a tightly defined driving cycle. A key feature of the evaluation is that the FTP is conducted after the catalyst has dealt with 50,000 - 100,000 miles of raw engine exhaust. During the FTP, 50 - 80% of the total pollutants emitted to the atmosphere by the vehicle occurs immediately following the startup of the engine when the engine block and manifold are cold, and the catalytic converter has not reached high conversion efficiencies, and are known as "cold start" emissions. The stringency of the regulations becomes evident when to qualify for either Low Emission Vehicle (LEV) or Ultra Low Emission Vehicle (ULEV) status, the hydrocarbon engine out emissions of 2.0 g/mile, typical for a six cylinder vehicle, must be reduced over the entire FTP by 97% and 99%, respectively. These regulations spurred a variety of new technology thrusts aimed at attacking the cold start hydrocarbons including electrically heated catalysts, hydrocarbon traps, exhaust gas burners, and close coupled catalysts (1).

The FTP test poses a unique catalytic challenge. After tens of thousands of startups and shutdowns, the three way conversion (TWC) catalyst must respond excellently, and rapidly to a wide range of operating conditions: Gas hourly space velocities and exhaust gas temperatures can both quickly jump two orders of magnitude in either direction, and the reactant species present in the exhaust gas vary moment-by-moment in composition, concentration, and relative ratio of oxidants to reductants. To meet these stringent emission levels three way conversion catalyst technologies have undergone a fundamental shift in composition and structure to address the needs for lower light-off temperatures, higher thermal durability, and better tolerance to sulfur poisoning. Much of the research effort has been devoted to mediating the primary deactivation mode for TWC catalysts, thermal sintering of both the precious metals and the base metal oxides. This talk will discuss the base metal and precious metal chemistries that have been blended into these durable heterogeneous catalysts for the efficient conversion of auto exhaust gases.

RESULTS AND DISCUSSION

Palladium has a well documented reputation for both hydrocarbon and CO oxidation (2). When our research began on palladium, this metal was known to damage rhodium's NOx efficiencies via the formation a palladium/rhodium alloy and by itself would give only moderate to low NOx conversion efficiencies. Since the functionality of the precious metal is strongly influenced by the surface upon which it sits, rare earth oxides were examined for their NOx promotional effects on palladium. The palladium-only catalysts were formulated utilizing washcoated cordierite (400 cpsi) substrates prepared from slurries containing mixtures of catalyst powders impregnated with palladium nitrate solutions and other oxide additives. All catalysts were aged to simulate in-use catalyst performance in a laboratory honeycomb reactor kept at 1223 K for 12 hr using a simulated auto exhaust gas stream or as full size pieces aged on engine test beds for 75 - 95 hr with a maximum bed temperature of 1193 K. Figures 1(a) and 1(b) summarize laboratory reactor data showing the promotional effects of the rare earth oxides on palladium for NOx reduction and CO oxidation respectively. In the absence of sulfur, the oxides of lanthanum, neodymium, and cerium improved NOx performance, whereas CO performance was only improved by the ceria. Interestingly, only ceria caused both the CO and NOx performances to increase as the temperature was raised. Apparently in the low temperature regime, the catalysis occurs on the palladium, whereas at higher temperatures the catalytic functionality of the ceria is activated and moves the palladium CO/NOx catalysis to a new performance level. However, the benefits of an intimate palladium-ceria interaction for CO/NOx proved a detriment for hydrocarbon activity, especially at elevated temperatures.

With lead levels in the U.S. fuel supply now well below 1 ppm, the most influential fuel component on catalyst performance is sulfur. Sulfur poses a number of challenges to the functioning of TWC catalysts via its interference with both precious metal and base metal function. The sulfur effect on the rare earth oxide promoters for the palladium-only catalysts was examined in the laboratory reactor. Figure 2 demonstrates how lean aging in the presence of sulfur lowered NOx activity via formation on an intermediate surface oxysulfate on the rare earth oxide. The loss in high temperature ceria performance was particularly notable, but fortunately the oxygen storage function can be restored by subsequent stoichiometric operation.

These findings were then used to create a new palladium-only catalyst architecture wherein the NOx and HC activities were segregated into separate catalytic layers. For best NOx performance the topcoat was formulated to contain the oxides of lanthanum, neodymium, and cerium so that their NOx promoting activity would have first access to the CO for NOx conversion. The bottom coat was kept ceria-free so as to maintain palladium's hydrocarbon and CO oxidation activity. A 0.69 liter palladium-only honeycomb catalyst, at 3.5 g/l palladium, was aged on an engine test bed using 300 ppm sulfur containing gasoline for 75 hr along with a production 5/1 platinum/rhodium catalyst at 1.41g/l of precious metal. The total FTP hydrocarbon/CO/NOx conversions efficiencies for the palladium-only catalyst on a 4.6 l vehicle was 95.1%/84.4%/84.1% versus the platinum-rhodium catalyst performance of 89.8%/80.5%/81.9%. The palladium catalyst gave the best hydrocarbon and NOx efficiencies and proved the catalyst formulation strategy of keeping the NOx reduction function separate from the hydrocarbon oxidation components..

The palladium-only catalyst showed sensitivity to the sulfur concentration in the exhaust gas in the low temperature regimes. In seeking to maintain the excellent hydrocarbon activity of palladium, but instill better sulfur tolerance into TWC catalysts, we investigated augmenting the best features of the palladium-only catalyst with platinum and rhodium. A Box-Behnken experimental design was employed with the metal loadings of 0 to 0.47 g/l for platinum, 1.41 to 5.65 g/l for palladium, and 0.09 to 0.37 g/l for rhodium. The catalysts were aged in 10% H_2O/ 90% air at 677 K for four hours. The catalysts were then evaluated on an engine test stand and the results of sweep test evaluations carried out at 673 K under stoichiometric conditions are summarized as contour performance plots for each pollutant in Figure 3. The contour plots show the metals work together synergistically to deal with the pollutants. Palladium makes the greatest contribution to the performance of the trimetal catalysts leading to improved performance for all three pollutants as the palladium content in the catalysts increases. The roles of platinum and rhodium can also be discerned from the contour plots where rhodium contributes to NOx conversion and the platinum, especially at high palladium levels contributes significantly to CO and NOx activity. The trimetal formulations also showed an improvement in sulfur tolerance. Experiments were conducted with a produetion 5/1 platinum/rhodium TWC eatalyst at 1.41 g/l of precious metal versus a trimetal catalyst designated ETM II with a precious metal loading of 3.71 g/l with a platinum/palladium/rhodium ratio of 1/14/1. Both catalysts were aged on a fuel cut aging cycle with an inlet temperature of 1173 K. FTP tests were conducted at various fuel content levels on a 2.0 liter vehicle fitted with multiport injectors. The catalyst volumes used in these experiments were approximately one-half what would be used in serial production to accentuate the impact of sulfur on TWC performance. At 300 ppm fuel sulfur, ETM II outperformed the platinum/rhodium catalyst for all three pollutants giving FTP g/mile emissions for hydrocarbons/CO/NOx of 0.79/3.4/1.05, whereas the platinum/rhodium catalyst gave 0.76/4.5/1.4. Sulfur had little impact on either catalyst for hydrocarbon conversion between sulfur concentrations of 50 - 300 ppm. However, when the sulfur content in the fuel was raised from 50 and 150 ppm both catalysts showed deterioration in CO and NOx conversion efficienecies. The platinum/rhodium catalyst allowing tailpipe CO and NOx emissions to increase from 3.4 to 4.4 g/mile and 1.15 to 1.45 g/mile, respectively. ETM II showed the same trends with CO increasing from 3.1 to 3.4 g/mile and NOx from 0.80 to 1.05 g/mile. Although ETM II proved more resilient to sulfur and the deactivation is reversible by high temperature exposure, continued research is required to develop strategies that mediate sulfur's impact on both the precious metal and oxygen storage components.

SUMMARY

The NOx performance of palladium-only TWC catalysts were substantially improved by bringing oxides of lanthanum, neodymium, and ceria into intimate contact with the palladium in the topcoat of a two coat catalyst formulation. The concepts used to improve the palladium-only catalyst were successfully applied to trimetal formulations which in turn proved to be more sulfur tolerant than corresponding platinum/rhodium catalyst.

REFERENCES
1. Burk, P.L., Hochmuth, J.K., Anderson, D.R., Sung, S., Punke, A., Dahle, U., Tauster, S.J., Tolentino, C.O., Rogalo, J., Miles, G., Mignano, M., and Niejako, M., Catalysis and Automotive Pollution Control III, eds. Frennet, A., Bastin, J.-M., Elsevier Science Publishers, 919 (1995).

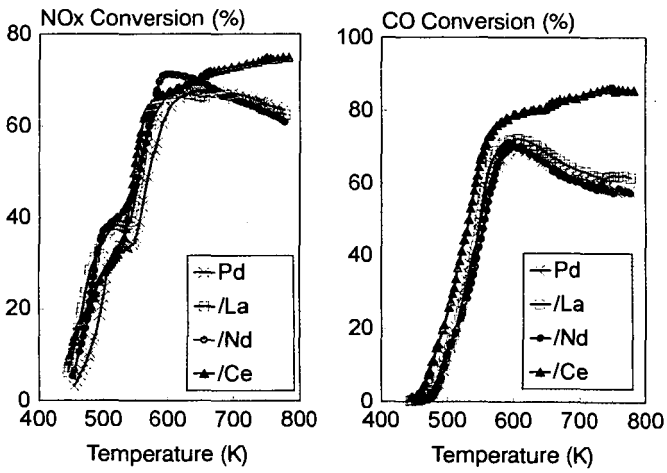
2. Taylor, K.C., Automobile Catalytic Converters in Catalysis Catal. Rev., 35(4) 457-481, 1993.

Table 1.
California's Low Emission Vehicle Program Certification Standards

	Federal Test Procedure (grams/mile)[a]		
Low Emission Vehicle Category	Nonmethane Organic Gases	CO	NOx
Transition	0.125	3.4	0.4
Low	0.075	3.4	0.2
Ultra Low	0.040	1.7	0.2
Zero	0.000	0.0	0.0

[a] Emissions after 50,000 miles

Figure 1 (a & b). Laboratory reactor data on aged Pd cores containing 1.75 g/l Pd and 12.2 g/l rare earth oxides



evaluated in a simulated exhaust gas of 0.75% CO, 0.25% H_2, 0.6% O_2, 1600 ppm NO, 280 ppm propene, 16.3% CO_2, 10% H_2O and N_2 balance at 50,000hr^{-1}.

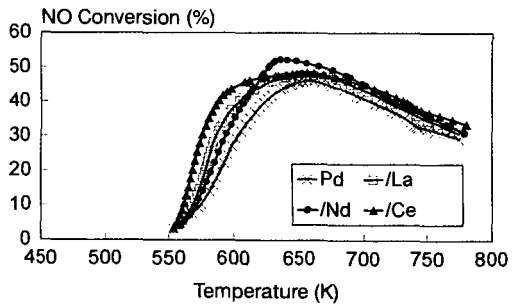


Figure 2. Laboratory reactor data on Pd cores containing 1.75 g/l Pd and 12.2 g/l rare earth oxides after aging in 10%H_2O/90% air and 40 ppm SO_2.

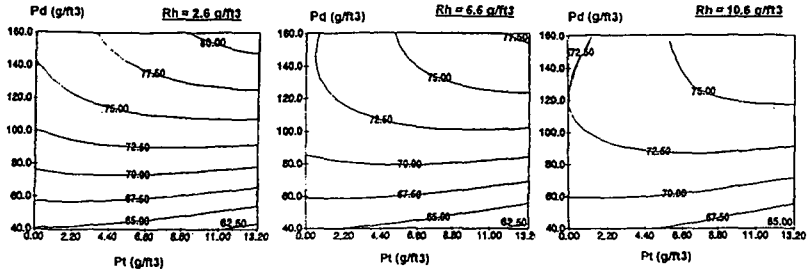


Figure 3(a). Hydrocarbon conversion activities.

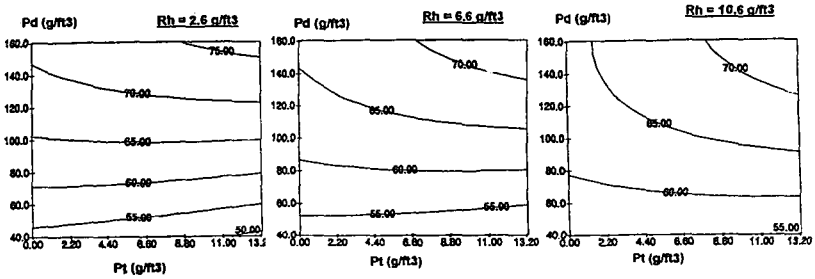


Figure 3(b). CO conversion activities.

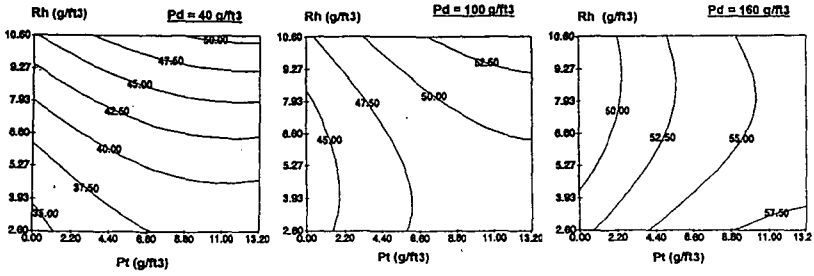


Figure 3(c). NO conversion activities.

THE CLEAN AIR ACT. IMPACT ON THE FUELS INDUSTRY. BACKGROUND . . . AND FUTURE?

James M. Kulakowski
Texaco Refining and Marketing Inc.
10 Universal City Plaza
Universal City, CA 91608

Key words: clean air act, air quality, fuels

The Clean Air Act - Presentation Topics (Slide 1)

Environmental regulations, including the Clean Air Act have a profound impact on the petroleum industry. For example, a recent study by the National Petroleum Council found that compliance with environment, health and safety regulations would cost the US refining and marketing industry some 37 billion dollars in the 1990s. This is greater than the entire 31 billion dollar asset base in 1990.

The federal Clean Air Act is arguably the most comprehensive single piece of legislation ever passed by Congress. The act was originally passed in 1963 and has had several revisions, the most recent being in 1990. The act has provisions that cover many pollutants and different sources of pollution.

This paper will only discuss limited portions of the clean air act that impact "mobile sources", that is fuels and vehicles. In addition to a discussion of the background for several of these issues, the paper provides a report of the current status. Finally, some recommendations are made to improve the flexibility in the act and the regulations it requires.

Setting Air Quality Goals (Slide 2)

The clean air act requires that the EPA set standards for air quality. The "criteria" pollutants include sulfur dioxide (SO_2), particulate matter, nitrogen dioxide (NOx), carbon monoxide (CO), ozone and lead. Areas that meet a standard for a pollutant are in "attainment", while those that do not are in "non-attainment". The clean air act specifies attainment dates for areas based on the level of a pollutant in a base year. For example, an area with ozone between 138 and 160 ppb ozone is classified as "moderate" and must attain the standard by 1996 while an area with greater than 280 ppb ozone is classified as "extreme" and must attain the standard by 2010. These ambient air quality standards also indicate how often an area can exceed the standard and remain in attainment. For example, the fourth 1 hour measurement over the 120 ppb ozone standard in 3 years puts an area in non-attainment. Stated another way, an area may exceed the standard 0.011% of the time and remain in attainment. The EPA has set standards for many pollutants but those that most impact mobile sources are ozone, carbon monoxide and particulate matter. It should be noted that EPA is considering a revision to the ozone standard. One revision being considered would increase the number of ozone non-attainment areas by 60%, from 79 to 119 based on estimates by the American Petroleum Institute.

Tropospheric (low level) ozone, or "summer smog" is a secondary pollutant, that is a pollutant which is formed in the atmosphere as opposed to being directly emitted from a source. The primary reactants are hydrocarbons and oxides of nitrogen, or NOx. Under certain conditions, these reactants, in the presence of sunlight which acts as a catalyst, react to form ozone. The atmospheric chemistry is very complex and is dependent on the ratio of hydrocarbon and NOx. In some areas, reducing one reactant can actually increase ozone. Tropospheric ozone should not be confused with stratospheric ozone, the subject of global warming concerns.

Carbon monoxide (CO) pollution is typically a winter time problem. CO is directly emitted, primarily from gasoline powered vehicles (as opposed to diesels).

Particulate matter is the fine particles suspended in the air. The current standard only covers particles less than 10 microns in diameter (PM10). This would include windblown dust as well as man made particulates. EPA is considering a new standard that would cover smaller particles and would focus more attention on man made particulate emissions.

State Implementation Plans (Slide 3)

States have the primary responsibility for meeting the federal air quality standards. They are required by the Clean Air Act to submit a plan to the EPA detailing how they will meet these standards. This plan is called the State Implementation Plan or SIP. Failure to submit a SIP can result in sanctions against an area in the form of lost federal highway funds. Actual demonstration of attainment is determined by monitoring ambient air quality.

Once a SIP is accepted by EPA, the regulations contained therein are federally enforceable.

Clean Air Act - Specific Control Measures (Slide 4)

The Clean Air Act includes mandated measures for certain areas. For example, the 9 areas with the highest ozone levels are required to include federal reformulated gasoline in their SIPs. Areas in non-attainment for CO are required to implement an oxygenated gasoline program. States with higher levels of ozone or CO are required to implement an enhanced vehicle inspection and maintenance program. The EPA-designed inspection and maintenance program is very specific as to type of test equipment, testing frequency and repair cost limits to earn a waver from the program.

Clean Air Act - Reformulated Gasoline (Slide 5)

The reformulated gasoline (RFG) program is contained in the clean air act. The act specifies several elements of the program, while leaving other key elements to the discretion of EPA. The statutory provisions for the RFG program contain both performance and prescriptive standards. For example, RFG must attain certain emission reductions, which are performance based, for toxic compounds, hydrocarbons and NOx. In addition, RFG is mandated to contain a minimum of 2.0 wt% oxygen and less than 1 volume % benzene. These are prescriptive standards that must be met irrespective of the emissions performance of the fuel.

As was noted earlier the 9 worst ozone areas are mandated to have RFG. The act also provides the opportunity for other non-attainment areas to "opt-in" to the program. Several areas did this, and subsequently desired to opt-out of the program. EPA allowed these "opt-outs", changing the overall volume of RFG demand. This change in RFG volume had the potential to drastically reduce the value of investments made for RFG compliance.

The enforcement program for RFG is very complex. In essence, it requires tracking of every molecule of gasoline from cradle to grave. Some of the elements include independent sampling and testing, year-end audits of production, and periodic reporting. Several of these provisions also apply to non-reformulated, or conventional, gasoline.

The RFG program includes two phases. The first phase, which was effective in 1995, includes statutorily developed targets for toxic and hydrocarbon emission reductions as well as a requirement that there be no increase in NOx emissions. In the second phase, EPA was given discretion over the level of the more stringent standards required by the act. EPA included a requirement for NOx reduction not originally conceived of in the act, in addition to further reductions in hydrocarbon and toxic emissions. This second phase is effective in 2000.

Clean Air Act - Regional Air Quality Organizations (Slide 6)

The Clean Air Act provides for several regional air quality organizations. This was done in recognition that some pollutants may be transported from one air basin to another and impact

air quality in these "downwind" areas. An example is the Ozone Transport Assessment Group which consists of representatives of the 37 states east of the Rocky Mountains. These states are evaluating a host of measures that could assist downwind ozone non-attainment areas to reach the standard. The analysis of transported pollutants and their impact on ozone is exceedingly complex and is only now beginning.

These organizations face an implicit political problem. Namely, it will be difficult for an elected official to pass a regulation which will cost his constituents when the benefits will be realized by others, perhaps in another state.

What's Going On Now? (Slide 7)

Several initiatives are underway which could further impact the fuel and automotive industries.

As mentioned above, the OTAG is looking at options, some of which include further fuel reformulation to address the issues related to pollutants transported from attainment to non-attainment areas.

EPA is considering revisions to the air quality standards for ozone and particulate matter. These standards are expected to be more stringent than the current standard and will put pressure on states to find more emission reductions.

EPA is considering revisions to allow attainment areas to opt-in to federal RFG. This could drastically increase the volume of RFG requirements. There are significant legal questions regarding whether the Clean Air Act grants EPA the authority to allow attainment area opt-ins.

California has included in its ozone SIP a measure that calls on EPA to adopt more stringent emissions standards nationwide for diesel trucks. This is driven by the fact that a significant portion of the Los Angeles NOx emissions inventory is sourced in out-of-state trucks visiting the area. EPA is working with California regulators and the engine manufacturers to determine whether these standards are attainable. At this point, it appears that changes to diesel fuel will not be immediately considered as a part of this strategy.

Finally, the auto makers are calling for a "nationwide fuel" that would have tighter specifications than those of the American Society for Testing Materials (ASTM) whose specifications are enforced by most states. The environmental necessity of such a fuel is questionable, as many areas of the country in which the fuel would be sold already attain federal air quality standards. Such a requirement would provide a fuel with less variability and assist the auto makers in the design of their vehicles, but would also represent a costly reformulation of gasoline for most refiners.

None of these initiatives were considered in the 37 billion dollar investment cited earlier. Needless to say, there will be continued pressure on the petroleum industry to deliver cleaner products to market.

What Needs to Happen? (Slide 8)

There are several areas where the Clean Air Act and the regulations it spawns can be improved. The items detailed below are but a few ideas.

Use of performance based standards will allow greater compliance flexibility and result in lower compliance cost. However, recent regulations that are advertised as performance based, are overlaid with elements of the command and control regulatory mind set. For example, if a party were to develop an additive that was demonstrated to reduce vehicle emissions to the same level as RFG, that party would have several regulatory hurdles to clear to certify that additive as a part of the RFG program. Hopefully, as more experience is gained in implementing performance based regulations, this will change.

The practice of air quality management needs better tools with which to do the job. An example is the Urban Airshed Model for predicting ozone. These models are tremendously complex, needing super computers to run efficiently. However, even with this complexity, their predictive capabilities are only marginal. Another area which needs improvement is the type of test used to characterize vehicle emissions. There are recognized shortfalls in the "federal test procedure". For example, it does not adequately test all driving modes (e. g. high acceleration) and is capped at 55 miles per hour. Finally, there needs to be testing of reformulated fuels on prototype advanced vehicles. Questions regarding the need for, and performance of these fuels of the future in the vehicles of the future have not been addressed.

There needs to be a consideration of risk-based air quality standards. Can our society afford to guarantee pristine air in all air basins regardless of the levels of population and economic activity? Risk-based, rather than health-based air quality standards will allow EPA to consider these types of questions.

Finally, there needs to be an explicit requirement that major regulations be subjected to some type of cost effectiveness test. To their credit, EPA generally has attempted to apply this type of analysis to fuels regulations. The California Clean Air Act contains such an explicit requirement. This has impacted the decisions of California regulators. It is time for all parties to recognize the need for air quality regulations to provide the necessary emissions reductions at the lowest possible cost.

The Clean Air Act.
Impact on the Fuels Industry.
Background . . . and Future?

Mike Kulakowski
Texaco Refining and Marketing
ACS Meeting - Orlando Florida
August 1996

Clean Air Act Presentation Topics

- **The Clean Air Act:**
  - Sets air quality goals
  - Outlines process by which states develop clean air programs
  - Outlines specific measures
    - Reformulated gasoline
    - Vehicle inspection and maintenance
  - Establishes regional air quality organizations

Air Quality Goals

- **Health-based standards set by EPA**
  - Ozone (formed by hydrocarbons and NOx)
  - Carbon monoxide
  - Particulate matter
- **Attainment deadlines set by initial air quality levels**
  - Higher levels of pollutant results in more time to attain standard
  - Example: Moderate ozone 1996. Extreme ozone 2010

State Implementation Plans (SIPs)

- **SIP details how an area will meet federal air quality standards**
  - Quantifiable
  - Enforceable
- **Regulations in SIP are federally enforceable**
- **Very specific guidance to states by EPA**
- **State maintains autonomy**

Clean Air Act . Specific Control Measures

- **Reformulated Gasoline (RFG)**
  - 9 mandatory areas specified in Act
  - Opt-in of ozone non-attainment areas allowed
- **Oxygenated Gasoline**
  - Winter carbon monoxide strategy
- **Vehicle inspection and maintenance**
  - Goal - On road vehicles' emission performance maintained at or near design levels

Clean Air Act Reformulated Gasoline

- **Performance standards**
  - Hydrocarbon/NOx/Toxic emissions
- **Prescriptive standards**
  - Oxygen/benzene fuel content
- **2 Phases to program**
  - Phase I - 1995
  - Phase II - 2000
- **"Anti-dumping" controls**
- **Very complex enforcement scheme**

Clean Air Act - Regional Air Quality Organizations

- **Examples**
  - Ozone Transport Commission (OTC)
  - Ozone Transport Assessment Group (OTAG)
  - Grand Canyon Visibility Task Force
- **Recognition of transported pollutants and precursors**
- **Allow for coordinated planning**
- **Political Issues**

What's Going on Now?

- **OTAG - Region-wide fuel standards?**
- **EPA reassessment of ozone and particulate matter standards**
- **EPA - Attainment area opt-in to RFG?**
- **EPA - Nationwide diesel engine standards?**
  - Driven by Los Angeles' ozone non-attainment
- **Automakers - desire for nationwide fuel specifications.**

Clean Air Act What Needs to Happen?

- **Better performance-based regulations**
  - More flexibility
  - Lower cost
  - Opportunities for new technologies
- **Better tools**
  - Air quality models
- **Risk-based air quality standards**
- **Explicit requirements for cost benefit tests for new regulations**

IMPACT OF FUEL CHARACTERISTICS ON IN-USE PERFORMANCE OF EXHAUST CATALYSTS

Donald. D. Beck
GM Research and Development Center
Warren, MI, 48090

William A. Short
GM Powertrain Group
Milford, MI, 48380

Keywords: in-use emissions, fuel impact, catalyst performance

ABSTRACT

In order to improve air quality, California has implemented a plan requiring low emission vehicles with advanced technology exhaust catalyst systems. These vehicles are certified and intended to operate on an advanced reformulated gasoline (California Phase 2). Other states have or intend to adopt a similar vehicle program, but although these vehicles will also be certified and designed for operation on the California Phase 2 gasoline, they will in practice be operated on a variety of gasolines, both reformulated and unreformulated. In some regions, enhanced inspection/maintenance tests will periodically be required which includes a test of the exhaust emission control system using a transient driving schedule. These tests will be performed using available commercial fuels, thus we have undertaken a study to determine the impact of several individual fuel properties on the resulting emissions produced during such a test. Properties varied individually include distillation, oxygenate content and sulfur level. In addition, the impact of each variable was measured at several different test temperatures to gain insight on the effect of ambient temperature on in-use emissions. We will discuss the result of these impacts and possible explanations based on additional insight gained from modal (second-by-second) emissions data as well as catalyst temperatures logged during the tests.

INTRODUCTION

One of the requirements for improving air quality called for by the Clean Air Act Amendments of 1990 involves the improvement of current programs in which vehicles are inspected in-use for emissions compliance. The enhancement as proposed by the Environmental Protection Agency for many non-attainment and neighboring areas requires vehicle owners to pass an emissions test at either a centralized inspection station or a qualified repair-and-test facility station in order to obtain a permit to register their vehicle [1]. In addition to the emissions test, the fuel vapor recovery system on the vehicle must also be checked for system integrity, and the OBD-II system checked for an activated MIL and stored fault codes.

One of the enhanced inspection/maintenance tests supported by the EPA involves an exhaust emissions compliance test in which tailpipe emissions of hydrocarbon, carbon monoxide and oxides of nitrogen are measured while the vehicle is driven over a transient schedule for 239 seconds [1-3]. This test, called the IM240 (inspection/maintenance 240) requires a relatively sophisticated chassis dynamometer and emissions measurement bench and is best administered at a centralized facility. It is already being utilized in enhanced I/M programs in Arizona and Colorado, and is being implemented in states such as Wisconsin, Maryland and Connecticut. Although alternative I/M tests may be adopted by other states, we will use the IM240 as the focus of this study.

As stated earlier, we are particularly interested in varying some fuel characteristics and the ambient test temperature to determine the impact on the resulting emissions. Such tests serve to probe the variety of test conditions that can be anticipated for I/M tests performed in the 49 states outside California, and allow us to compare such tests to those that would more closely represent conditions anticipated within California, recognizing that California has adopted a strictly controlled low-sulfur reformulated fuel to be sold state-wide [4]. This may be particularly important for Low Emission Vehicles which may be held to strict emission standards, even in in-use tests. Although these vehicles were originally proposed by California as part of their state plan to achieve better air quality, member states of the Ozone Transport Region (13 Northeast states and the District of Columbia) have or are in the process of considering adoption of the California Low Emission Vehicle program to meet their state implementation plan (SIP) requirements, without also adopting the California Reformulated Fuel Program.

For this study, then, we compare IM240 tests performed using a pre-production Transitional Low Emission Vehicle under relatively moderate temperatures using low-sulfur-content California reformulated phase 2 fuel to similar tests performed under a range of

temperatures and using federal fuel surrogates with various distillation, oxygenate and sulfur content properties.

EXPERIMENTAL

The vehicle used for the enhanced inspection maintenance testing was a 2.2 L OHV Corsica equipped with a 4-speed automatic transmission and linear EGR. The vehicle was configured as a production-intent 1996 MY California TLEV and included a complete OBD-II system. The inlet of the single underfloor converter used with this vehicle is located approximately 50" from the exhaust manifold, and the converter itself is 110 cubic inches in volume, containing 2 oval cross section monoliths of the same size. The forward monolith contained a palladium technology washcoat, while the rear contained platinum and rhodium. A single converter was used for these tests and had accumulated 89,000 miles in customer service. This converter was evaluated for FTP performance using certification fuel on this vehicle with the following results: 0.089 g/mi THC, 2.28 g/mi CO and 0.32 g/mi NOx (all values comply with TLEV standards).

The vehicle was also configured with a converter inlet tap for modal engine-out emissions measurements. In addition, several locations in the exhaust stream and in the converter monolith beds were instrumented with thermocouples for monitoring the temperature at those locations. A portable laptop computer equipped with a serial port and an analog/digital conversion board was used to log selected engine operation and temperature data in real time during the IM240 test schedule.

The reference fuel used for this study conformed to the California Phase II reformulated gasoline standards, and contained sulfur at a level of 32 ppm. A relatively high vapor pressure fuel used as Wintertime surrogate contained sulfur at a higher level (485 ppm) and was used both with and without oxygenate modifications. A lower vapor pressure fuel used as a Summertime surrogate also contained sulfur at a higher level (480 ppm) and was also used with and without oxygenate modifications. MTBE was used in any oxygenate modifications. A summary of the fuel properties is listed in Table 1.

IM240 tests described in this study were conducted using a single 48" dynamometer roller which was electrically-loaded. This test site was capable of collecting both bag (integrated) and modal (second-by-second) emissions data, and is located in an environmental cell capable of test temperatures between -9°C and 36°C. Testing at low temperature with the high volatility Winter fuel simulates an IM240 test that would be encountered in much of the U.S. (outside of California) in the Wintertime. In practice the IM240 test may be run in a heated/closed bay; however, the vehicle will be exposed to cold temperatures during the urban driving phase and time at idle, and may also encounter these conditions during the exhaust test itself. Since the climate in the highly populated areas of California is moderate for the entire year, testing at ambient temperature with the strictly controlled California reformulated fuel simulates a California IM240 test for a majority of the state and for most of the year. Whenever fuels were changed in these tests, a purge procedure was followed to allow the vehicle sufficient exposure to the new fuel prior to conducting tests.

The IM240 emission tests were conducted using a procedure described in a previous publication [5] and was used to simulate typical customer driving history prior to an I/M test and to obtain highly repeatable results. This procedure generally included a soak period followed by an urban driving phase (bag II of the FTP), followed by an idle for 15 minutes, and finally the IM240 test (the 15 min waiting period for an IM test is considered to be representative of a typical wait time in the field [6]). For the purpose of this discussion we will focus on the modal emissions data generated during the IM240 portion of this study. Following the IM240 test, the vehicle was left to soak at the test temperature for at least 1 h with the fan directed into the radiator, and the entire test procedure (FTP Bag 2 + idle + IM240) could then be repeated. This entire procedure was repeated to produce two complete IM240 measurements for each fuel and time at idle matrix element.

RESULTS AND DISCUSSION

The first set of IM240 tests were run using the California Phase 2 reformulated fuel at 74°F (23°C). We found that the engine-out FTP emissions of 1.7 g/mi HC, 8.9 g/mi CO and 1.9 g/mi NOx were relatively consistent with the engine-out IM240 emissions of 1.3 g/mi HC, 9.2 g/mi CO and 2.7 g/mi NOx. The relative agreement in the engine-out emissions values provides further support for the IM240 test procedure as a relatively rapid surrogate for the FTP test. The tailpipe emissions performance on the IM240 was the following: 0.119 g/mi THC, 1.633 g/mi CO and 0.384 g/mi NOx, which also compare favorably with the FTP results at 0.089 g/mi THC, 2.28 g/mi CO and 0.32 g/mi NOx. In this case, the IM240 results were 34% greater for THC, 40% greater for CO and 20% greater for NOx when compared to an FTP test result. As will become apparent later, the IM240 results were consistently larger than the corresponding value obtained during an FTP test.

Our discussion will now turn to IM240 test conditions that can be commonly expected when Wintertime oxygenated fuel is available, typically November to March. In this study we ran IM240 tests at 20°F (-7°C), 40°F (4°C) and 60°F (16°C) to cover a wide range of ambient temperatures that can be expected for most of the country during the Winter. Although the numerical results are not reported here, the engine-out emissions obtained for these tests at the three temperatures mentioned above generally remained the same for all test temperatures and was similar to the results obtained using the California reformulated fuel, with the exception of NOx, which increased by roughly 45% as the temperature was decreased to -7°C from 16°C. The tailpipe emissions, however, are clearly impacted by both fuel property and test temperature. For example, test results obtained using the federal fuel at 16°C are between 40 and 100% greater (88% for HC, 85% for CO and 45% for NOx) when compared to test results using the California fuel at 20°C. Tailpipe emissions continue to increase dramatically with further decreases in test temperature, even with the same federal fuel being used for the tests. At -7°C, the tailpipe emissions levels are between 200% and 300% greater than the results obtained using California fuel at a test temperature of 20°C (specifically, 275% for HC, 275% for CO and 230% for NOx). Although the observed increase in the tailpipe emissions for NOx can be partly attributable to an increase in engine-out NOx levels under colder test conditions, most of the observed increase in HC, CO and NOx tailpipe emissions can be attributable to differences in the fuel properties and test conditions. As will be suggested by the following results, fuel oxygenate can influence tailpipe emissions, but not at all temperatures. At the lowest temperature used in this study (-7°C), tailpipe emissions are affected more by sulfur content and distillation.

A similar set of IM240 tests were also performed at 20°F (-7°C), 40°F (4°C) and 60°F (16°C) using the same fuel base, but with no oxygenate present. Tests using this fuel also resulted in increased tailpipe emissions when compared to tests using the California Phase 2 Reformulated fuel, and the increases were generally similar when compared with the oxygenated Wintertime fuel, except that CO was affected more and NOx was affected less with the non-oxygenated fuel at test temperatures above -7°C. Tests using this fuel at 16°C, for example, produced 0.205 g/mi HC, 4.38 g/mi CO and 0.401 g/mi NOx. This represents increases of 88% for HC, 150% for CO and ~0% for NOx when compared to the California fuel. Further decreases in test temperature to -7°C did result in further increases in tailpipe emissions, reaching 0.392 g/mi HC, 6.55 g/mi CO and 1.37 g/mi NOx, which represents increases of 260% for HC, 273% for CO and 230% for NOx. At moderate test temperatures of 16°C and 4°C, then, the addition of oxygenate to the fuel does reduce CO emissions as demonstrated in prior published studies. At -7°C, however, the presence of oxygenate in the fuel has no influence on the tailpipe emissions. A summary of the tailpipe results for both types of higher vapor pressure fuels are shown in Figure 1.

The observed IM240 tailpipe emission increases attributable to fuel and test condition effects are in good agreement with our previously reported study [5] of IM240 tests in which a similar test comparison was made between tests using commercial Winter fuel and California Phase 2 fuel using a similar TLEV. These results are in contrast to the typically cited 10-20% in-use emissions increases predicted by MOBIL5a to account for differences in the fuel properties, the latter forming the basis for the most stringent IM240 cutpoint tables. As mentioned above, although the increase in the tailpipe emissions for NOx can be partly attributable to an increase in engine-out NOx levels under colder test conditions, most of the observed increase in HC, CO and NOx tailpipe emissions can be attributable to factors which directly influence catalytic converter performance. It turns out that such factors are not related to converter temperature, since this was found to be similar regardless of the test fuel or test temperature, but rather to a combination of the influence of sulfur, operating air/fuel ratio, and HC composition and combustion characteristics of the fuel on converter efficiency as suggested by the modal data. A thorough discussion of these impacts is beyond the scope of this paper, but will be discussed more completely in a future paper.

Similar tests were conducted using a lower vapor pressure fuel to represent a summertime blend, but with an elevated sulfur (475 ppm) level. Tests were conducted both with and without oxygenate (~11% MTBE), and at test temperatures of 20°C, 16°C, and 4°C (the fuel drivability was poor at -7°C, thus tests were not run at that temperature). We found that in general, use of this fuel did not affect engine-out emissions when compared to the California Reformulated fuel (except that NOx was increased by 20% at 4°C, similar to the Wintertime fuel), but increases in the tailpipe emissions were observed. These increases, however, were not as significant as with the Wintertime fuel for the same test temperature. For example, tests at 16°C resulted in increases of ~30% for HC, 55% for CO, and 25% for NOx when compared to similar tests at 20° using the California fuel. Further decreases in test temperature did result in further increases in tailpipe emissions, but these increases

were not as significant as with the Wintertime fuel. When a similar set of tests were run with the oxygenated version of this fuel, a similar trend was observed in that the tailpipe emissions increased with decreasing test temperature. However, the magnitude of the increase was smaller than observed for the non-oxygenated version of this fuel for a given test temperature. In summary, then, of the four federal fuel surrogates used in these tests, the highest tailpipe emissions were generally observed for vehicle operation at relatively low temperature (-7°C) using the high vapor pressure (or Wintertime) fuel blend with oxygenate present. The lowest tailpipe emissions were observed for vehicle operation at relatively moderate (~20°C) temperature using a lower vapor pressure fuel (Summertime) with oxygenate present. For comparison, the California phase 2 reformulated fuel produced even lower tailpipe emissions when tested under a moderate temperature condition. As we have mentioned previously, modal data indicates that the large observed difference in the tailpipe emissions (particularly hydrocarbon) when comparing low vapor pressure fuel tested at moderate temperature with high vapor pressure fuel tested at relatively low temperature can be attributed primarily to effects of the operating air/fuel ratio and the fuel hydrocarbon composition and combustion characteristics on converter efficiency. Colder test conditions lead to poorer air/fuel control, while higher vapor pressure fuels contain a larger relative percentage of relatively unreactive short-chained saturated hydrocarbons, part of which escapes combustion in the engine and/or oxidation in the catalyst. The presence of higher sulfur levels appears to accentuate these effects.

SUMMARY

We have investigated the effects of several fuel properties and test temperatures on the IM240 tailpipe emissions performance of a 1996 Corsica TLEV. We found that in all cases, the lowest emissions were obtained using a California phase 2 reformulated gasoline in tests at 20°C, while tests using federal fuel surrogates all produced higher tailpipe emissions, and the highest emissions were produced when high vapor pressure fuels were used under relatively cold temperatures (-7°C). In the latter case, the tailpipe emissions were between 200% and 300% greater than similar tests run using the California fuel at 20°C. The large increase in the emissions observed when tests were run on the federal fuels can be attributable to a combination of higher sulfur levels, lower test temperature, and different fuel hydrocarbon makeup (indicated by high vs. low vapor pressure).

REFERENCES

1. "Inspection/Maintenance Program Requirements", Federal Register Notice, November 5, 1992; 40 CFR, Part 51, Subpart S.

2. "High-Tech I/M Test Procedures, Emission Standards, Quality Control Requirements, and Equipment Specifications: Final Technical Guidance", U.S.E.P.A. Document No. EPA-AA-EPSD-IM-93-1, April, 1994.

3. W. M. Pidgeon and N. Dobie, "The IM240 Transient I/M Dynamometer Driving Schedule and the Composite I/M Test Procedure", U.S.E.P.A. Report No. EPA-AA-TSS-91-1, January, 1991.

4. Title 13, California Code of Regulations, Sections 2262.1-2262.7.

5. D. D. Beck, W. A. Short, T. A. Angelos and R. R. Dils, "IM240 Emissions tests with a 2.2 L Corsica TLEV", SAE Paper No. 942001, 1994.

6. R. Babcock, presentation at the Tenth Annual Clean Air Act Conference, Estes Park, Colorado, September 27-29, 1994.

Table 1.
Summary of Selected Properties of Test Fuels

Fuel Description	Vapor Pressure (psi)	Oxygenate (% vol.MTBE)	Sulfur (ppm)	Saturates/Olefins/Aromatics (%)
California Phase 2 federal fuel	6.6	11.1	29	73 / 5 / 22
(high vapor pressure) federal fuel	11.8	*	480	71 / 7 / 22
(low vapor pressure)	7.9	*	475	74 / 4 / 22

* Each of these fuels were used with no MTBE added and with 11.5% vol. MTBE added.

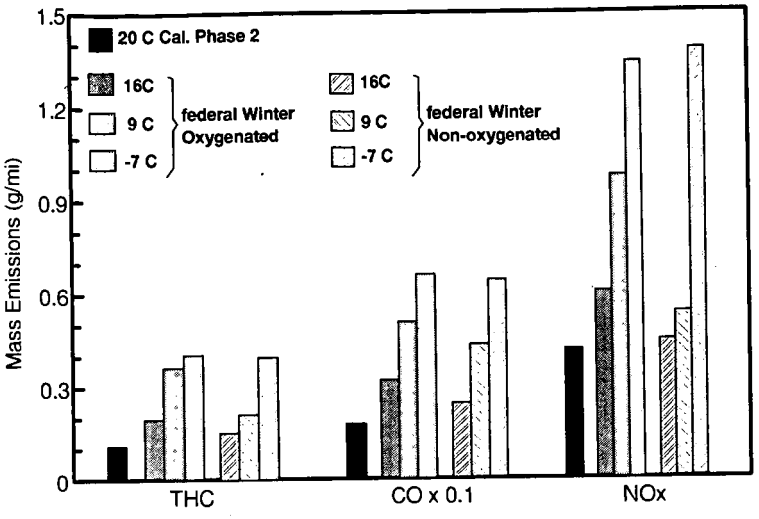


Figure 1. Comparison of IM240 tailpipe emissions at various test temperatures and for operation on different fuels.

FUEL REFORMULATION AND EMISSIONS IN EUROPE AND JAPAN

H.J.Lovink
Catalyst Consultant
Aletta Jacobslaan 17
3818 LP Amersfoort
The Netherlands

Keywords: Diesel,Gasoline,Emissions Improvements,Europe,Japan.

A. Introduction

In the drive for a cleaner environment of the transportation sector not only the vehicles,but also the fuels are studied for further improvements. Europe and Japan are no exceptions,although in motorgasolines the US is clearly leading.
While diesel is only 17% of US motor fuels,it is more important in Europe,Japan and the rest of the world with some 45%-plus,and so is its reformulation.

Recently an extensive European Oil/Auto test program,called EPEFE has been completed in order to decide on new "Europe-wide"specs. for both diesel and motorgasolines.
Later this year the European Commission and Parliament will decide on the specifics,the time schedule etc. after having heard all parties concerned.

Much earlier work and study has preceded this;but in the final judgement both any extra CO_2 and costeffectiveness will be considered,plus special local problems (big cities:Milan,Athens,etc.)

CONCAWE, the "Oil Companies' European Organization for Environment,Health and Safety",
established in 1963,has played as important role in this and earlier test programmes as well as ACEA (Auto Co's) and national institutes active in the collective interest.

The Japanese situation,on-the-ground at least as difficult as southern Europe/California,is different:
- --Tight regulations on emissions,
- --A severe testing schedule,and young vehicle population,
- --Good fuels,see later.

Their extensive statistics,reporting "road-side SOx and -NOx" demonstrate the results of their efforts.As in Holland and Germany SOx and HC are coming down, but NOx stays high. Because yes,we all are driving more and more using ever more motor fuels!

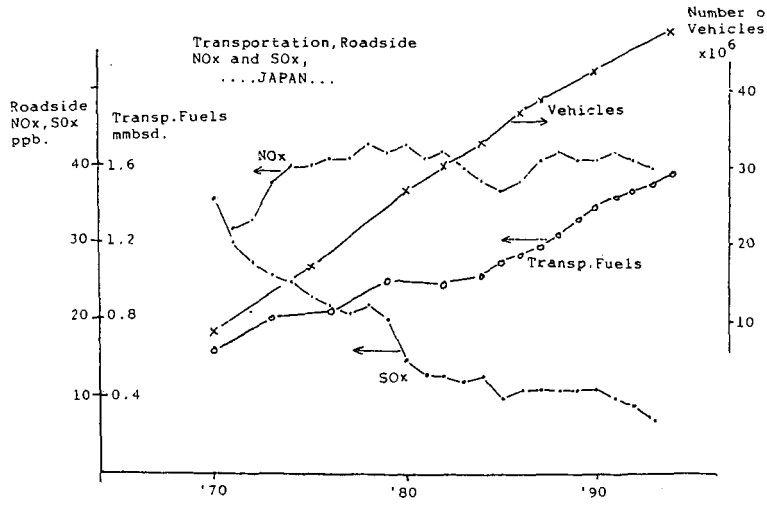


fig.1

B . Diesel Fuel Studies in Europe

During the last decade the improvement of diesel engines and fuel has been high on the agendas of both manufacturers and refiners. Like in gasoline, most progress has been made in engine design, and most recently, with catalytic soot filters.

In the recent past CONCAWE had already shown that:

a) The Cetane Number is the most important parameter for most emissions; much more than Density, Aromatics, and T90. The latter have varying effects of some 5% at best within the limits of commercial interest.
b) Catalytic filters are able to reduce CO/HC/PM by some 20-25%, moreover all fuel effects become smaller, see lit.2&3.

The European Programme on Emissions, Fuels and Engine Technology, EPEFE, described above, had selected for experiments those areas that had not been covered sufficiently earlier or elsewhere in the US and Japan.
An outstanding feature of their recent series is the use of engines with "year 2000"-technology, so not today's engines.
This choice shows clearly in the level of emissions, Table 1, in particular the low HC/CO/PM -values. They could even be comparable to California TLEV 's.

However, in these vehicles the effects of variations in diesel-properties , even over a wide range are limited, see table no 1.
When comparing the results in Light Duty and Heavy Duty vehicles table 2, the plusses and minusses do not even match always, so a "Solomon's Judgement" is needed!

Table 3 gives the principle characteristics of the average diesel fuels of the US, Japan and Europe, plus some of the "talked about" changes in specs, which now have entered the environmental-economic-political arena in Brussels.
The costs of diesel reformulation has been calculated for several scenarios by CONCAWE, lit.5; table 6 has been derived from a still "modest" scenario. A cetane spec. change to 58 min indeed looks unlikely seen the costs of widespread deep aromatics hydrogenation and the extra energy-to-CO_2!

C. Motorgasolines Studies, Europe

With all the work done in this particular area in the US and the results of actions in California, the EPEFE program has only tried to fill in some blank spaces because of the different car population, and the speedier driving habits: the European tests are now containing a 120 km/hr. section.
Here also cars with "yr-2000" engines have been used, which shows up in their low av. emissions. One car has such a good, flexible air:fuel ratio controler that its NOx is 0.07 g/km for all fuels. Its other emissions were also so low that no fuel quality effects could be detected! Table 4 has the results of this section of the recent European tests. Earlier US conclusions regarding Sulphur were confirmed; all other parameters gave "plusses & minusses"

Although the general feeling is strongly in favor of "one percent Benzene max, these and other health risk studies suggest this is not necessary now and in the nearby future.

Table 5 compares the average values of motor gasoline inspections of the US, Japan and Europe. (only some essential items)
The octanes are slightly higher in Europe, even of the lead-free grades. All new cars are designed for RON/MON=95/85.
Re-setting the specs to the values "talked about" will have enormous consequences for the refining industry.
A "reg-neg" process, as in the US, leading to Simple and Complex models is not feasible in Europe. A gradual introduction of new specifications, allowing the industry time to invest, both the auto makers and the refining side, is most likely.

Table 6 summarizes the costs of the above depicted targets of reformulation of both gasoline and diesel fuel: virtually every refinery will need new equipment, particularly hydrocrackers and hydrotreating/hydrogenation units. (from lit.5)

In Japan a further study as a result of the "1995 White Paper on the Environment" is expected to lead shortly to new legislation. However, an increasing part of acid rain seems to come from the rapidly developing neighboring countries!

D. Concluding Remarks

--Reformulation of motorfuels in Europe is now under general scrutiny; tighter specs on both diesel and gasoline are expected, rather than "complex or simple models".

--Major improvements can only be expected from new engine-and exhaust treatment technology; first indicationsare that also here some 10% reduction of emissions can be obtained from so-called cleaner fuels.

--NOx from diesel engines could be the remaining problem; a catalytic solution is highly desirable! (See lit.6)

Literature:

1--Petroleum Industry in Japan,1995, by "The Japanese Committee for World Petroleum Congresses" (fax +81-3-5395-5384)

2--Concawe Report no.92/54

3-- " " no.94/55&56

4--EPEFE report,Diesel Project, WEFA conf.'95 .M.Hublin

5--Concawe Report no.95/54

6--Motor Vehicle Pollution, Reduction Strategies beyond 2010. OECD-publication 1995. Paris.

TABLE 1
Diesel Reformulation Test results
European -EPEFE test program with
"Yr.-2000 engines and catalysts"

		grams per km.			
A Light Duty Vehicles		CO	HC	NOx	PM
-- Emissions level of testvehicles		0.45	0.10	0.55	0.06
-- Vehicle Euro-specs. '95/'96		2.1	0.25	0.62	0.12
California TLEV		2.1	0.15	0.3	0.08
-- Major Improvements by Reformulations	%	25[3]	25[3]	3.4[2]	19[1]
B Heavy Duty Vehicles		grams per KWh			
-- Test vehicle level		0.59	6.3	3.6	3.6
-- Euro-specs.		4.0	1.1	7.0	0.15
-- Calif.'94 level		11.0	1.0	6.7	0.11
-- Major Improvements by Reformulation	%	10[3]	6.3[3]	3.6[1]	3.6[2]

C. Fuels Programme:

1)Density decrease: 0.855 to 0.828
2) Poly Aromatics%: from 8 to 1%
3)Cetane Number : " 50 to 58
4) T-95,degrees C : 370 to 325

TABLE 2
Comparison of effects of fuel properties
..Light and Heavy Duty Vehicles...

		CO	HC	NOx	PM
DENSITY	LD*	-17.1%	-18.9%	+1.4%	-19.4%
855-828 kg/m3	HD**	+5.0%	+14.3%	-3.6%	-1.6%**
poly-aromatics	LD*	+4.0%	+5.5%	-3.4%	-5.2%
8-1%	HD**	-0.1%***	-4.0%	-1.7%	-3.6%
cetane number	LD*	-25.3%	-26.3%	-0.2%***	+5.2%
50-58	HD**	-10.3%	-6.3%	-0.6%	-0.1%***
T95	LD*	-1.8%***	+3.4%***	+4.6%	-6.9%
370-325 deg C	HD**	+6.6%	+13.4%	-1.7%	0.0%***

- * ECE+EUDC cycle
- ** ECE R49 13-mode cycle
- *** Statistically non significant

TABLE 3

Average Properties of Diesel Fuels
(excl. color,cold flow,stab.etc.)

	US	JAPAN	EUROPE	Changes "Talked-about"
Density,g/ml	0.848	0.838	0.840	"down"
Aromatics %	30	23	25	25 max.
Poly- Arom.%	-	-	4-6	?
Cetanes:				
-number	46	55	51	55 min.
-index	47	57	53	-
Sulphur ppm	----------500 max---------			"down"?
T20 C	240	240	215	-
T50 C	270	260	265	-
T95 C	315	345	360	?

TABLE 4

Motor Gasoline Reformulation Europe,
Results of the recent EPEFE test programme

	CO	HC	NOx
	---------grams/km -------		
Test Vehicles used, "Yr. 2000 technology"	1.41	0.16	0.18 a)
Euro/EFTA-specs.	2.0	0.25	0.12
California TLEV	2.1	0.16	0.62
Japan '94	2.1	0.15	0.24

Maximum Improvements:

1) S from 400 to 20 ppm : all emissions down 10%!
2) Aromatics from 50% to 20% : CO/HC down 10%: NOx up 10%.
3) E100 °C 60% to 40% : no effect.
4) T90 °C 185 to 165 : CO/HC down 5%: NOx,see 2);no change.
5) Benzene 2.5%-0.95% : down from 5% to 3,5% in HC emitted.

a) One vehicle,with a new very good A-F ratio controler tested 0.07 g NOx per km!

TABLE 5

Typical Properties -Motor Gasolines '94
.....Averages,Summer.....

	US Baseline '90	US RFG-II	JAPAN	EUROPE
RVP. psi	7.8	6.7	8	7-9
Sulphur,ppm	338	140	40	300
Oxygen %	-	2.1	0.5	0.6
Aromatics %	28.6	25	30	35
Olefins %	10.8	12	16	12
Benzene %	1.6	0.95	2.5	2.1
RON/MON	-----95/84-----		94/84	96.5/86
T50 °F	207	200	204	200
T90 °F	332	313	300	320
E200°F,vol %	46	49	51	45
E300°F,vol %	83	87	91	84

"Europe" may reduce in) stages the following) items:

Sulphur to 100 ppm max.
Aromatics to 25 % max.
Olefins to 10 % max.
Benzene to 1 % max.
Oxygen to 1.5% min.

TABLE 6

Economic Impact of Reformulation
of Gasoline and Diesel-- Europe.
(Concawe Report no.95/54,yr.2000)

A) Diesel - quality,appr.table 3;200 ppm S; 100×10^6 tons/yr.

	Capital charge	All other op.costs	Total	Extra CO_2 from Refining, kg/ ton
	----------$/mTon--------			
Cetane No. =55	15	5.5	20.5	50
Cetane No. =58	20	19	39	350

Compare with the late '95 prices of av. diesel fuel:
..in bulk ,tax free: $/ton 170
..at the pump,
incl. all taxes : " 700-1200

B) Motor Gasoline -quality table 5; quantity 125×10^6 tons/yr.

Capital Charge,excl.for MTBE: $/ton.. 16
Other fixed & variables " .. 6
" 22+

Compare with:..'95 market price, excl. taxes: $/ton 200
"At-the pump" incl. taxes...: " 1200-1500!

AQIRP AND EPEFE - A COMPARISON OF THE PROGRAMS AND THEIR RESULTS

Brian H. Rippon
Ford Motor Company
The American Road, Room 255 WHQ
Dearborn, Michigan 48121-1899

Keywords: Gasoline, Emissions, AQIRP, EPEFE

ABSTRACT

Since it was established in 1989 by 14 oil companies and three domestic automakers, the U.S. Auto/Oil Air Quality Improvement Research Program (AQIRP) has made substantial progress in developing an information base of fuel and vehicle effects on emissions. This program was the largest and most comprehensive project of this nature ever attempted. More recently, the European Programme on Emissions, Fuels, and Engine Technologies (EPEFE) marked an unprecedented cooperation between the European motor and oil industries to extend the information on fuels and engine technologies for the European continent. AQIRP and EPEFE were the first large scale systematic efforts to develop extensive data on the inter-relationships among fuel composition, vehicles, emissions, and air quality. This scientifically based information will allow legislators and regulators to design cost effective methods with which to achieve their clean air goals.

INTRODUCTION

Motor vehicles have historically been viewed as one of the main sources of ozone and carbon monoxide pollution in the United States. But over the past three decades, the contribution of the automobile to urban pollution has been steadily decreasing. Nationwide, emissions of HC, CO, and NO_x from on-road vehicles have declined in absolute quantity, as well as relative to other sources of air pollution.

Even though today's new vehicles produce substantially less ozone-forming HC and NO_x emissions than the new vehicles of 25 years ago, ozone concentrations in 33 urban areas remain above the current federal air quality standard. In the same time frame, nine cities were above the carbon monoxide standard. While these numbers represent a major improvement from prior years, significant future reductions in emissions from a variety of sources – stationary and mobile – will be required to help meet the ozone standard in the remaining areas.

Similarly, many European cities are experiencing unique and significant problems caused by the use of diesel fuel by both passenger cars and trucks and the consequent increased burden of particulate matter. Reductions from many sources, including mobile, will be needed to tackle the air quality problems.

Mobile source reductions will be achieved in many ways. Future vehicle systems are being designed to achieve lower emissions. In addition, gasoline and diesel fuels are being reformulated in some areas to reduce emissions from both existing and future vehicles. Alternative fuels also may play a role in decreasing emissions.

In the past, the successful achievement of these goals has been hampered by a lack of scientific knowledge in a variety of areas. For instance, one specific need has been comprehensive data about the interrelationships among fuel composition, vehicles, emissions, and air quality. The U.S. Auto/Oil Air Quality Improvement Research Program (AQIRP) and the European Programme on Emissions, Fuels, and Engine Technologies (EPEFE) were created to develop that knowledge.

AQIRP

The Auto/Oil Air Quality Improvement Research Program (AQIRP) was established in 1989 by 14 oil companies and three domestic automakers. The program has made great progress in developing an information base on fuel and vehicle effects on emissions. The overall objective of AQIRP has been to provide this data to help legislators and regulators achieve the nation's clean air goals through a research program that included:

(1) Estimation of potential reductions in vehicle emissions from changes in fuel composition.
(2) Estimation of potential improvements in air quality - primarily ozone - and fuel reformulation.
(3) Estimation of the relative cost effectiveness of some fuel/vehicle systems.

This program was the largest and most comprehensive project of this nature ever attempted.

Over the course of the six-year program, AQIRP conducted more than 5,000 emissions tests using over 80 fuel compositions in over 100 vehicles. The tests measured engine, tailpipe, evaporative, and running-loss emissions, and quantified the concentrations of 153 different organic compounds plus oxides of nitrogen (NO_x) and carbon monoxide (CO). Using the 175 megabytes of data generated by these tests, AQIRP has developed an extensive data base of fuel composition and vehicle effects on emissions.

The emissions data were employed in air-quality modeling studies for New York City, Los Angeles, and either Chicago or Dallas-Fort Worth, using state-of-the-science models and emissions inventories. In these studies, AQIRP focused on fuel and vehicle changes that would reduce predicted ozone air pollution. Extensive refinery modeling studies were also conducted to develop cost estimates for producing various research gasoline formulations.

AQIRP found that the following changes can be effective in reducing vehicle mass emissions and/or improving ozone air quality.

- Lowering the aromatic content of gasoline lowers toxic emissions.
- Lowering the T_{90} and/or T_{50} (boiling range) of gasoline reduces ozone and exhaust HC emissions.
- Lowering the sulfur content of gasoline decreases exhaust emissions of HC, CO, NO_x, toxics, and ozone.
- Lowering the olefin content of gasoline reduces NO_x and ozone, but increases exhaust HC emissions.
- Adding oxygenates to gasoline reduces CO in older and current technology vehicles.
- Lowering the Reid vapor pressure (RVP) of gasoline reduces evaporative emissions, exhaust HC and CO emissions, and ozone.
- Identifying and repairing high-emitting vehicles reduces evaporative emissions, exhaust emissions and ozone.
- The introduction of newer vehicle technology has resulted in decreases in regulated emissions, toxics and ozone.

EPEFE

The European Programme on Emissions, Fuels, and Engine Technologies (EPEFE) began in 1994. It was an essential part of the European Auto-Oil Programme which constituted a new approach in setting environmental legislation and which harnessed the expertise of the European Commission, industry, and consultants in Europe. The intent of the Auto-Oil Programme was to identify which new measures may be required to meet rational air quality objectives in the most cost effective way, derived from scientifically sound data. The EPEFE program was designed to extend the information on the relationships between fuel properties and engine technologies and to quantify the reduction in in-use emissions that can be achieved by combining advanced fuels with the vehicle/engine technologies under development for the year 2000. Specifically, EPEFE included:

(1) Assessment of the current state of emissions relationships available from fuels/vehicles.
(2) Generation of new data for the air quality modeling program in Europe.
(3) Estimation of the cost benefit of fuel/vehicle technologies relative to the year 2000 requirements.

During its two years of activity, EPEFE examined 12 gasolines in 16 gasoline-powered vehicles, and 11 diesel fuels in 19 light duty vehicles and 5 heavy-duty engines. More than 2000 emissions tests were performed, providing over 500,000 measurements of HC, CO, and NOx exhaust emissions, and diesel-generated particulates.

The emissions data from EPEFE were used in air quality modeling studies for seven European cities including London, Cologne, Hague, Lyon, Athens, Milan, and Madrid. Additional studies are also being conducted to identify the most cost effective way to implement the findings.

The following EPEFE results confirm that both fuels and engine technologies are important determinants of motor vehicle emission levels.

* Lowering the aromatic content of gasoline decreases exhaust HC and CO.

* Reducing the aromatic level of gasoline reduces CO_2 at each E100 volatility level with no impact on fuel consumption.

* Increasing the mid-range volatility of gasoline decreases exhaust HC.

* Decreasing the T90 (boiling range) of gasoline reduces light-duty PM and heavy-duty exhaust NO_x.

* Lowering the sulfur level of gasoline reduces exhaust HC, CO, and NO_x.

* Decreasing the density of diesel fuel reduces light-duty diesel HC, CO, and PM, and reduces heavy-duty diesel NO_x.

* Decreasing the polyaromatic content of diesel fuel reduces light-duty diesel NO_x and PM, heavy-duty diesel HC, NO_x and PM.

* Increasing the cetane rating of diesel fuel reduces diesel HC and CO.

Conclusions About AQIRP and EPEFE

These landmark cooperative research programs have contributed enormously to the understanding of the relationships between fuels and vehicles.

AQIRP was a milestone in cooperatively developing a sound technical database for use by regulators. In addition to developing new test techniques for measuring and speciating emissions, the program also made significant contributions to the development of atmospheric models and the understanding of how fuels impact atmospheric pollution.

The California Air Resources Board (CARB) has adopted gasoline specifications based on program findings. CARB and the U.S. Environmental Protection Agency have both made use of AQIRP's data in developing mathematical models to predict emission changes from changes in fuel properties. AQIRP data will continue to influence decisions on air quality improvement control options for years to come.

EPEFE, which was inspired by the AQIRP, is providing similar benefits for Europe as it provides a scientific basis for the establishment of cost effective European exhaust emission standards for the year 2000. The program brought together European Union Commission, the European oil industry, and the European auto industry for the first time in a large scale cooperative research program. The program enhanced the body of data already in existence within Europe and from AQIRP to expand on the relationships between fuels and automotive emissions. The EPEFE process aided the search for a balanced set of measures which could help meet the European Union's air quality objectives.

These programs have shown that:

* Oil and automotive industries can work together effectively on important research objectives.

* Both programs have made important findings and have substantially increased the body of knowledge of vehicle/fuel effects.

* Matching fuels to vehicles is critical. They form a "system" which maximizes the potential of each.

* Controlling mobile source air pollution requires a detailed understanding of fuel/vehicle systems, inventories, atmospheric chemistry, and cost effectiveness.

Results (Gasoline)

AQIRP

- Aromatics (per vol. % decrease) FTP Cycle

HC	CO	NOx
-0.2	-0.5	NS

Note: AQIRP results are for "Current" Technology vehicles unless otherwise noted.

EPEFE

- Aromatics (per vol. % decrease)* MVEG 11-second Cycle
  - * @ E100 = 35%

HC	CO	NOx
-1.1	-0.6	+0.5

  - * @ E100 = 50%

HC	CO	NOx
-0.4	-0.6	+0.3

  - * @ E100 = 65%

HC	CO	NOx
-0.3	-0.6	+0.1

* 5% CO_2 reduction from high to low aromatics

Results (Gasoline cont.)

AQIRP

- T_{90} (per 5°F decrease)

HC	CO	NOx
-1.4	NS	+0.3

- T_{50} (per 5°F decrease)*

HC	CO	NOx
-2.1	NS	+1.3

* HC results for 180 - 240°F range
CO and NOx results for 185 - 215°F range

EPEFE

- T_{90} - held constant in EPEFE matrix for each level of E100
- E-100 (per % evaporated)
  - * E-100 @ 20% Aromatics

HC	CO	NOx
-0.8	-0.1	+0.2

  - * E100 @ 35% Aromatics

HC	CO	NOx
-1.2	-0.1	+0.4

  - * E100 @ 50% Aromatics

HC	CO	NOx
-1.4	-0.1	+0.7

Results (Gasoline cont.)

AQIRP

- Sulfur (per 50 ppm decrease - not linear) FTP Cycle

HC	CO	NOx
-2.2 to -2.9	-2.4 to -2.8	-1 to -1.5

EPEFE

- Sulfur (per 50 ppm decrease)
  - * MVEG Cycle - composite new 11 sec. idle

HC	CO	NOx
-1.2	-1.2	-1.4

  - * EUDC Portion (Sulfur results)

HC	CO	NOx
-7.1	-5.8	-2.8

  - * ECE Portion (Sulfur results)

HC	CO	NOx
NS	-0.9	NS

Results (Gasoline cont.)

AQIRP

- Olefins (per vol. % decrease)

HC	CO	NOx
+0.4	NS	-0.4

- Oxygenate (per wt. % increase)

HC	CO	NOx
-1.9	-4.1	NS

- RVP (per psi decrease)

HC	CO	NOx
-4%	-9%	NS

EPEFE

Results (Diesel)

AQIRP

- Diesel - not tested

EPEFE

- Reducing Density 0.855 - 0.828 g/l

HC	CO	NOx	PM
		LD	
-18.9	-17.7	+1.4	-19.4
		HD	
+14.3	+5	-3.6	NS

- Reducing Polyaromatics 8 to 1% m/m

		LD	
+5.5	+4	-3.4	-5.2
		HD	
-4	NS	-1.7	-3.6

Results (Diesel cont.)

AQIRP

- Diesel - not tested

EPEFE

- Increasing Cetane number 50 to 58

HC	CO	NOx	PM
		LD	
-26.3	-25.3	NS	+5.2
		HD	
-6.3	-10.3	-0.6	NS

- Reducing T_{95} from 295 - 370°C

		LD	
NS	-1.8	+4.6	-6.5
		HD	
+13.4	+6.6	-1.7	NS

CHEMICAL KINETICS OF CETANE NUMBER IMPROVING AGENTS

K.Hashimoto, Y.Akutsu, M.Arai and M.Tamura

Department of Chemical System Engineering, School of Engineering, The University of Tokyo

7-3-1 Hongo Bunkyo-ku Tokyo 113 Japan

INTRODUCTION

The increasing demand for diesel fuels has resulted in the use of greater percentage of cracked distillates having poor ignition properties. The ignition properties of diesel fuels can be rated in terms of their cetane number and diesel fuels having low cetane number may have poor ignition properties such as diesel knock, difficulties to start engines in the cold weather and so on. Such diesel fuels need cetane number improving agents. In the 1940s and 1950s alkyl nitrates, alkyl nitrites and organic peroxides were found to be effective cetane number improving additives (1). Our recent study suggests that free radicals produced from thermal decomposition just before ignition should have an important role to improve their ignition properties (2). However no studies on the reaction mechanism for improving effect of these additives have been attempted because of complex nature of spontaneous ignition reaction of hydrocarbons. In order to clarify the reaction mechanism for improving effects of cetane number improving agents. We here have attempted to simulate the spontaneous ignition of n-butane as a model compound in the presence of alkyl nitrites as cetane number improving agents.

CALCULATION METHOD

Calculations are performed using Chemkin and Senkin programs from the Sandia National Laboratories. Simulation reactions are assumed to be carried at under adiabatic condition at constant volume. Kozima's model (3) partly revised by adding thermal decomposition of cetane number improving agents was used for spontaneous ignition of n-butane in the presence of cetane number improving agents. Batt and the other's kinetic data (4) were used for simulation of the thermal decomposition of alkyl nitrites. Unknown thermochemical data were estimated by using the THERM program (5).

RESULT AND DISCUSSION

Addition effects of n-amyl nitrite addition on ignition delay period of n-butane are shown in Fig.1. Fig.1 shows that n-amyl nitrite addition to n-butane reduces ignition

delay period suggesting that this reaction model can simulate the effect of cetane number improving agents on ignition delay period.

Fig.2 shows the mechanism for thermal decomposition of n-amyl nitrite. In the thermal decomposition of n-amyl nitrite, weak N-O bond is dissociated to produce n-amyloxy radical and nitric oxide. Then beta-fission of n-amyloxy radical immediately produce n-butyl radical. Under the preignition conditions of n-butane, n-amyl nitrite may be thermally decomposed to induce complex radical reactions that enhance the n-butane ignition reactions. Thus n-amyl nitrite would reduce the ignition delay period of n-butane spontaneous ignition.

Fig.3 and Fig.4 show effects of initial pressure and temperature on ignition delay period of n-butane in the presence of n-amyl nitrite respectively.

Table I shows additive effect of n-amyl nitrite, n-propyl nitrite and t-amyl nitrite on ignition delay of n-butane. The effect of n-amyl nitrite is larger than that of n-propyl nitrite and t-amyl nitrite. Our previous experimental results (2) show that the effect of n-amyl nitrite on cetane number is larger than that of n-propyl nitrite and t-amyl nitrite. The present calculation results would be much in agreement with the experimental results.

Fig.5 shows the mechanism for thermal decomposition of n-propyl nitrite and t-amyl nitrite. Thermal decomposition of n-propyl nitrite and t-amyl nitrite can produce ethyl radical. We suggest that larger ignition delay reduction effect of n-amyl nitrite than that of n-propyl nitrite and t-amyl nitrite should be due to larger reactivity of n-butyl radicals than ethyl radicals under the preignition condition of n-butane.

CONCLUSION

In order to clarify the reaction mechanism for improving effects of cetane number improving agents, we have attempted to simulate the spontaneous ignition of n-butane in the presence of alkyl nitrites. As a result, it is shown that n-alkyl nitrite can reduce the ignition delay period of n-butane. It is known that cetane number improving agents decompose to produce alkyl radicals under operation conditions of diesel engine. We suggest that alkyl radicals produced would enhance the pre-ignition reactions of hydrocarbons to reduce ignition delay period. And it is also shown that the cetane number improving agents having higher cetane number can reduce the ignition delay period of n-butane more effectively. We also suggest that more reactive radicals should have larger effects on reduction of ignition delay period.

LITERATURE CITED

(1)Robbins, W.E., Audette, R.R. and Reynolds, N.E., SAE Quart. Trans., 5, 404 (1951)

(2)Hashimoto, K., Kawakatsu, Y., Arai, M. and Tamura, M., J. Jpn. Inst. Energy, 74, 200(1995)

(3)Kojima, S., Combust. Flame, 99, 87(1994)

(4)Batt, L. and Milne, R.T., Int. J. Chem. Kinet., 8, 59(1976)

(5)Ritter, E.R. and Bozzelli, J.W., Int. J. Chem. Kinet., 23, 767(1991)

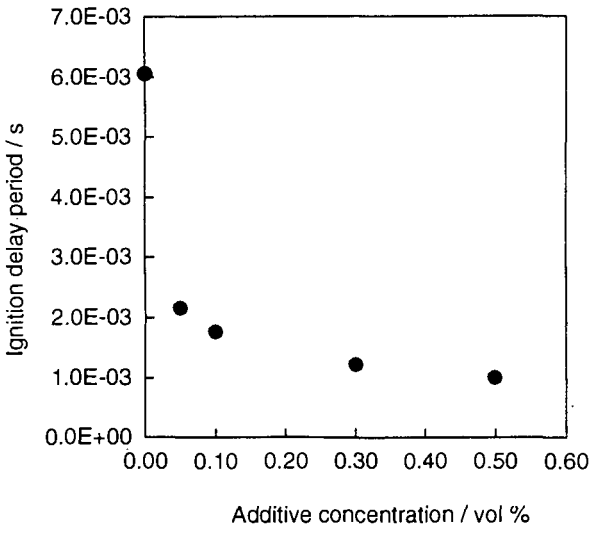


Fig.1 Ignition delay period vs additive concentration

Additive : n-Amyl nitrite

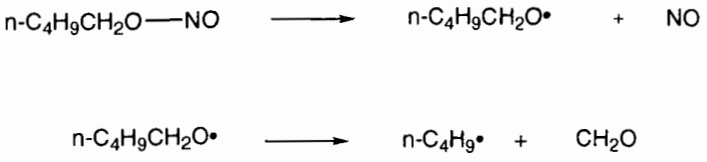


Fig.2 Mechanism for thermal decomposition n-amyl nitrite

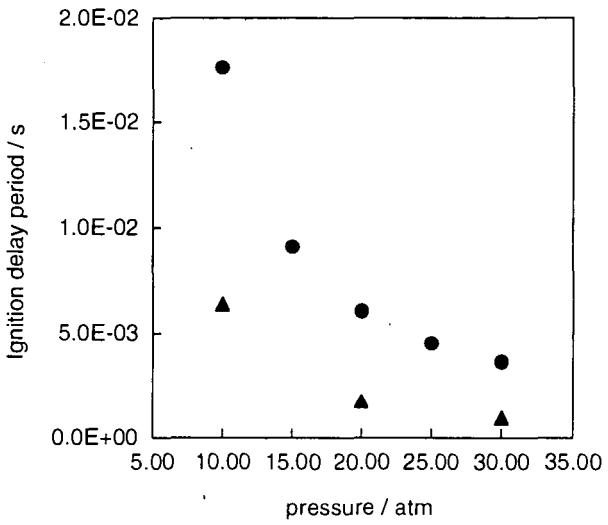


Fig.3 Ignition delay period vs initial pressure

Initial temperature : 800K

● No additive

▲ n-Amyl nitrite 0.1 vol %

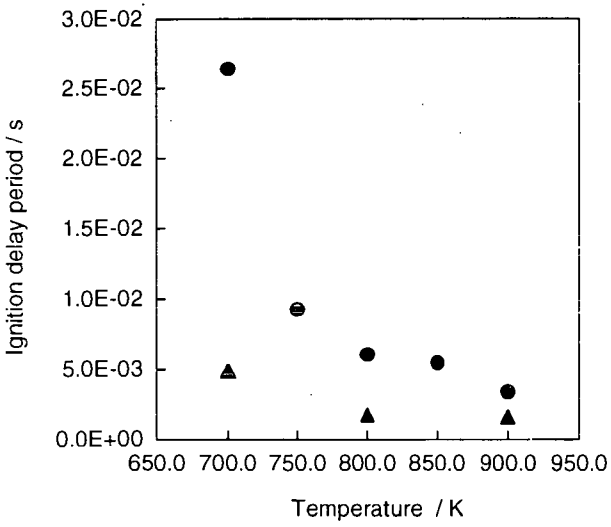


Fig.4 Ignition delay period vs initial temperature

Initial pressure : 20atm

● No additive

▲ n-Amyl nitrite 0.1 vol %

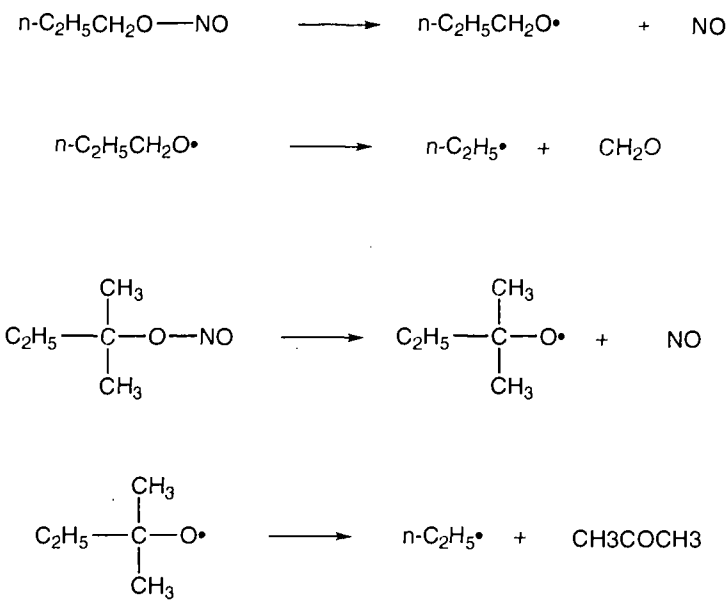


Fig.5 Mechanism for thermal decomposition of n-propyl and t-amyl nitrite

Table 1 Ignition delay period in spontaneous ignition of n-butane in the presence of additives

Additive concentration : 0.1 vol %
Initial temperature : 800K
Initial pressure : 20atm

Additives	Ignition delay period / 10^{-3}s
n-Amyl nitrite	1.76
t-Amyl nitrite	1.92
n-Propyl nitrite	1.92

THE PERFORMANCE OF DI-TERTIARY-BUTYL PEROXIDE AS CETANE IMPROVER IN DIESEL FUELS

Manish K. Nandi
ARCO Chemical Company, Newtown Square, PA 19073.

Key Words: Diesel Fuel; Cetane Improver; Heavy-duty diesel engine emissions

Abstract

Increasing the cetane number of diesel fuel, either by lowering aromatic content of the fuel through hydrotreating and/or by addition of chemical cetane improvers, is a cost-effective option to reduce diesel engine emissions. It is generally recognized that chemical cetane improvement additives represent a low cost alternative to aromatic reduction. Although both methods significantly reduce engine emissions, deep hydrotreating tends to adversely affect some fuel properties. We are evaluating the performance of a peroxide based cetane improver for diesel fuel. A comparison is made between the performance of di-t-butyl peroxide and the conventional cetane improver, 2-ethylhexyl nitrate. Correlation between the cetane response of the peroxide with the different fuel properties is discussed. Both the additives significantly reduce all regulated and unregulated emissions including NOx emissions. The NOx emissions from the peroxide treated fuels are consistently lower than those for the nitrate treated fuels at similar cetane level. The chemistry for the synthesis of di-t-butyl peroxide is discussed.

Introduction

The implementation of stringent diesel engine emissions regulations is growing worldwide. In the United States, the 1990 Clean Air Act mandates lowering oxides of nitrogen (NOx) emissions to 4.0 grams per horsepower-hour (g/hp-hr) in 1998. Future proposals by EPA call for a further reduction of a combined NOx and HC to 2.5 g/hp-hr for the year 2004 for heavy-duty trucks and buses. Such emission reduction will require a combination of new engine technology and economically viable low emission diesel fuels.

It is widely accepted that increasing the cetane number represents one option for production of cleaner burning diesel fuels. Numerous studies, including the Coordinating Research Council VE-1 and VE-10 programs, have demonstrated that increasing the cetane number of the fuel significantly reduces all the regulated emissions.[1] Increasing the cetane number of diesel fuel can be achieved by lowering aromatic content of the fuel through hydrotreating and/or by addition of chemical cetane improvers. It is generally recognized that chemical cetane improvement additives represent a low cost alternative to obtaining higher cetane number achieved through aromatic reduction. Moreover, deep hydrotreating to reduce aromatics tend to adversely affect some fuel properties, e.g., waxing and cold flow.[2]

Chemical cetane improvers are those compounds that readily decompose to form free-radicals, which in-turn promote the rate of initiation. This increased rate of chain initiation leads to improved ignition characteristics of diesel fuel. Chemicals selected from alkyl nitrates, certain peroxides, tetraazoles, and thioaldehydes can serve as cetane improvers. Due to their low costs, alkyl nitrates have played the most significant role in commercial use. 2-Ethylhexyl nitrate (EHN) has been used as a commercial cetane improver for a number of years and today is the predominant cetane improving additive in the marketplace. Di-tertiary-butyl peroxide (DTBP) was first recognized as an effective cetane improver in the 1940's.[3] Due to its higher cost, DTBP has not achieved the same wide spread usage as EHN. New technology has been developed by ARCO Chemical Company that will substantially reduce the cost of DTBP to a level comparable to that of EHN. Moreover, DTBP has a potential advantage over alkyl nitrates in reducing NOx emissions since it does not contain nitrogen.[4] DTBP is currently used in limited amounts in an after market fuel treatment package.[5] This fuel additive package containing DTBP, has been evaluated, certified and approved for use by the Department of the Navy.[6]

Synthesis

Dialkyl peroxides can be synthesized by the reaction of an alcohol and/or an olefin with an organic hydroperoxide, using an acidic catalyst. In the process developed at ARCO Chemical Company, t-butyl alcohol and/or isobutylene is reacted with t-butyl hydroperoxide in the presence of an acidic resin catalyst.[7]

Cetane Response

Cetane response, which may be defined as the relationship between the change in cetane number of the fuel and the concentration of the cetane improver, is a key factor for commercial acceptance of a cetane improver. We have studied, in details, the cetane response of DTBP in a variety of commercial diesel as well as in various diesel fuel blend stocks, worldwide.[8] The relative effectiveness of DTBP versus the commercial cetane enhancer, EHN, was determined in numerous base fuels with varying fuel properties as well as different blend stocks.

On an average, DTBP is between 85% to 90% as effective as EHN in increasing cetane number of diesel fuels.

It is also very important to understand the relation between the diesel fuel composition or properties and its cetane response for DTBP. We have developed a predictive cetane response equation for DTBP based on various fuel properties, viz., aromatics, mid-range distillation point (T_{50}), flash point, and pour point. The regression equation describing the change in cetane number due to the addition of DTBP is:

$$\Delta C = (39.8727 + 0.02335 * Z_2 - 0.0823 * Z_3 + 0.1405 * Z_4 - 0.0777 * Z_5) + (-0.1176 * Z_3 + 0.0430 * Z_5) * X + (-0.1190 * Z_4 - 0.0113 * Z_5) * X^2$$

with $R^2 = 0.889$ and RMSE = 1.6846

where ΔC = expected change in cetane number,
X = concentration of additive (wt%)
Z_2 = flash point (°F)
Z_3 = aromatics (wt%)
Z_4 = pour point (°F)
Z_5 = mid-range distillation point, T_{50} (°F)

Thus, given the values for appropriate fuel properties, the above equation can be used to predict, within their limits of uncertainty, the expected change in cetane number due to the addition of a specific amount of DTBP. However, it is recommended that this equation be used within the valid range of the experimental data used to generate it and the results not be extrapolated beyond an additive concentration of 0.75 wt%. Since this equation reduces to a simple quadratic form on substitution of the fuel properties, it can also readily be solved to determine the amount of additive required to increase the cetane number of the fuel by a desired amount.

Although the cetane response equation was generated based on several fuel properties, statistically, the two most influential fuel parameters were the aromatic content and the mid-range distillation temperature (T_{50}).

The cetane response of DTBP was inversely related to the aromatic content of the fuel. Thus, low aromatic fuels will respond well to the additive. On the contrary, fuels with high aromatic content or highly aromatic blend stocks like light cycle oil (LCO) or light cycle gas oil (LCGO) will respond very poorly to cetane improvers. Indeed, a highly aromatic (87%) LCGO blend stock did not respond at all to either of the cetane improvers, DTBP or EHN. Assuming the cetane improvers react through formation of free radicals to accelerate combustion, this low response for the aromatics may be attributed to the higher activation energy required for the nitrate or peroxide free radicals to react with an aromatic fragment compared to a aliphatic hydrocarbon fragment of the fuel. This, in fact, follows a similar trend for natural cetane for different fuel fragments, where aromatics have poor natural cetane numbers while straight chain aliphatic hydrocarbons have the highest natural cetane numbers.

The relationship between the cetane response of the two additives for the different fuels and the mid-range distillation temperature of the fuel is less clearly understood. In general, it was observed that the lighter fuels respond better to cetane improvers compared to the heavier fuels, especially at low additive levels. More work is needed to understand this effect.

It must be emphasized that although the cetane response equation, described here, use the base diesel fuels' properties to compute the expected change in its cetane number, the relationship between these changes and the fuel properties are by no means causal. Rather, the fuel properties are merely manifestations of some other more fundamental attributes of the fuel.

Engine Emissions

Numerous studies by the Coordinating Research Council and others have shown that increasing the cetane number through the use of additives reduces all regulated emissions.[1] The Coordinating Research Council's VE-10 program addressed the effect of cetane additives on diesel emissions.[9] The first part of this study, using two different 1994 heavy-duty engine technologies, demonstrated that the use of cetane improvement additives produces significant reduction in carbon monoxide and oxides of nitrogen emissions, with hydrocarbon and particulate matter being either unaffected or slightly reduced. Cetane additives including DTBP and EHN at levels up to 1.25 wt% were included in the continuation of this study using 1998 engine technology. Even using 1998 engine technology, having lower emissions than any diesel engine on the road today, increasing the cetane number with either EHN or DTBP reduced all engine emissions.

ARCO Chemical Company has conducted extensive testing on the effects of cetane additives on emissions from heavy-duty diesel engines.[10] This testing was conducted on a 1991 Detroit Diesel Series 60 heavy-duty diesel engine, typical of an engine currently in service, using the 1992 Federal Test Procedures for transient testing of heavy-duty engines. A total of four

fuels, representative of those currently commercially available, were used. The properties of the four test fuels are described in Table 1. One of these fuels, designated C, is a standard 2-D fuel, which meets the requirements for a diesel engine certification fuel as defined in CFR 86.1313-94(b)(2). The effects of both the cetane improvers, including a mixture of the two additives in fuel C, on engine emissions are summarized in Table 2.

Table 1: Test Fuels Properties

Property	Fuels			
	A	B	C	D
Cetane Number (D613)	46	41	43	38
Aromatics, vol% (D1319)	20	25	32	35
Sulfur, wt%	0.01	0.01	0.03	0.01
API Gravity, (D287)	37.9	35.4	35.7	33.4
Distillation Range (D86)				
IBP, °C	200	168	178	181
50% Point (T50), °C	243	247	259	248
EP, °C	328	333	334	344

Table 2: Effect of Cetane Improver on Regulated Emissions

Base Fuel	Additive	Additive Level (wt%)	Increase in Cetane Number	Hydrocarbon	Carbon Monoxide	NOx	Particulate Matter
A	EHN	0.40	10	- 41%	- 27%	- 1.9%	11%
	DTBP	0.50	11	- 43%	- 29%	- 2.2%	12%
B	EHN	0.70	15	- 59%	- 40%	- 2.8%	0.7%
	DTBP	0.80	16	- 58%	- 40%	- 3.9%	2.5%
C	EHN	0.60	9	- 60%	- 37%	- 1.9%	2%
	DTBP	0.65	10	- 59%	- 36%	- 5%	- 4%
	EHN/DTBP	0.31	10	- 59%	- 37%	- 2.6%	- 6.6%
D	EHN	0.65	10	- 75%	- 47%	- 2.8%	- 40%
	DTBP	0.75	10	- 77%	- 49%	- 3.3%	- 40%

As evident from the results increase in cetane number can significantly reduce hydrocarbon and carbon monoxide emissions in all the fuels. The NOx emission from the cetane improved fuels showed a small reduction compared to the base fuels, with the limited number of tests used for these study. The NOx emissions from the peroxide treated fuels, although not statistically significant, were lower than that from the nitrate treated fuels, in each of the base fuels. The peroxide produced about 0.5% to 3% lower NOx when compared to the nitrate at the same cetane level. These results indicate that when blended to comparable cetane numbers, DTBP produces lower NOx emissions than EHN. This trend is not only observed in this work but also in other works with different fuels, different engines, and using different international test protocols.

Gaseous Toxics Emissions

The use of a cetane enhancer substantially reduces the four gaseous toxic emissions of 1,3-butadiene, benzene, formaldehyde, and acetaldehyde.[10] Typical reductions in these four gaseous toxic emissions achievable by increasing the cetane number of a fuel by ten numbers, which on average required 0.65% cetane improver, vary from 30% to 70%.

Ozone Forming Potential

Complete speciation of the volatile hydrocarbons, aldehydes and ketones into C_1-C_{12} fractions was included as part the test program conducted by ARCO Chemical Company. Using standard Minimum Incremental Reactivity (MIR) values, the ozone forming potential was calculated.[10] Typical reductions in the ground level ozone forming potential achieved by a ten number increase in cetane using additives is between 50% to 75%. With ground level ozone, a major cause of smog, becoming an increasing problem in metropolitan areas, significant reductions

in ground level ozone attributed to diesel engine emissions can be obtained through the use of cetane improvers.

Soluble Organic Fraction of Particulate Matter

The use of DTBP produces substantial reductions in the soluble organic fraction of the particulate matter.[10] These reductions in the soluble organic fraction of the particulate matter are expected in-turn to reduce the emissions of both polyaromatic hydrocarbons and nitrated polyaromatic hydrocarbons.

Thermal and Oxidative Stability

A cetane improvement additive that is thermally or oxidatively unstable under actual conditions impacts on the fuel quality and could lead to poor engine performance resulting from the decrease in cetane number or fuel degradation. Thus, for commercial acceptance the peroxide based cetane improvement additives must be stable, thermally and oxidatively, at actual use temperatures.

The thermal stability of DTBP was demonstrated by determining the effects of heating on the treated fuels and also by measurement of the decomposition rates in a low sulfur diesel fuel.[8] A fuel treated with DTBP showed no statistically significant loss in cetane number after heating for 100 hours at 92°C. The half-life for DTBP at 70°C in diesel fuel is in excess of 10,000 hours, with greater than 97% of the additive remaining after nearly 700 hours. Even at 100°C, the half-life of DTBP in diesel fuel is over 300 hours. Even though the rate of thermal decomposition of the peroxide is five to ten times faster than the nitrate, the peroxide additive is very stable under typical fuel system temperatures.

Additives can cause diesel fuel degradation if they are not oxidatively stable. The oxidative stability of DTBP was demonstrated by the standard ASTM methods. Both the accelerated oxidative stability test (D274)[12] and the long term storage stability test (D4625)[13] did not show any gum formation in most of the diesel fuels tested. In some inherently unstable fuels degradation was observed. But they can be controlled easily by addition of very small amount of antioxidants.

Conclusion

Increasing the cetane number by addition of chemical cetane improvement additive is a cost effective way to produce cleaner burning diesel fuels. A peroxide based cetane improvement additive, di-t-butyl peroxide, can be very effective as a cetane improver. DTBP can be synthesized cheaply by the reacting isobutylene with t-butyl hydro peroxide. It is comparable in performance to 2-ethylhexyl nitrate, the cetane improver currently used commercially. DTBP has the potential of reducing NOx emissions more that the nitrate at comparable cetane level. The additive is thermally and oxidatively stable in diesel fuels at typical fuel systems temperatures.

Acknowledgement

The author wishes to thank Dr. Frank Liotta, Dr. Jeffrey McFarland, Dr. Daniel Pourreau, Dr. David Jacobs, Mr. Richard Englebach and Mr. Michael Camesi at ARCO Chemical Company for their contribution to the project. The author also thanks Mr. Dan M. Montalvo and Mr. Terry L. Ullman at Southwest Research Institute (SwRI) for their help in the emissions testing program.

References

1.(a) Nandi, M.; Jacobs, D. C.; Kesling, H. S.; Liotta, F. J. ; "The Performance of a Peroxide-based Cetane improvement Additive in Different Diesels Fuels"; SAE 942019, October 1994 and references there.

(b) Nandi, M. K.; Jacobs, D. C.; "Cetane Response of Different Di-tertiary-butyl Peroxide in different diesel fuels; SAE Paper 952369; October 95 and references there.

2. Stocky, T.; "Role of Cetane Improvers", Reformulated Diesel Symposium, Toronto, Canada; 1994.

Marriott, M.; "Diesel Quality and Emissions - European Experiences",. Reformulated Diesel Symposium, Toronto, Canada; 1994.

3. Wiles, Q.T.; Bishop, E.T.; Devlin, P. A.; Hopper, F. C.; Schroeder, C.W.; Vaughan, W. E.; Ind. and Eng. Chem., 1679 (1949).

4.(a) Reference1(a).

(b) Liotta, F. J.; "A Peroxide Based Cetane Improvement Additive with Favorable Fuel Blending Properties", SAE Paper 932767, October 1993.

(c) Coordinating Research Council VE-10 Project Final Report (1995).

5. U.S. Patent 4797134.

6. Department of The Navy, Office of The Assistant Deputy Under Secretary (Safety and Survivability), Justification and Approval No. 94-004, (10/14/93).

7. US Patent 5,371,298.

8. Reference 1(b).

9. Coordinating Research Council VE-10 Project Final Report (1995).

10. References 1(a) and 3(b).

11. Kesling, H. S.; Liotta, F. J.; Nandi, M. K.; "The Thermal Stability of a Peroxide-Based Cetane Improvement Additive"; SAE Paper 941017; March, 1994.

12. Reference 4(b).

13. Internal ARCO Chemical Company results.

DIMETHYL CARBONATE PRODUCTION FOR FUEL ADDITIVES.

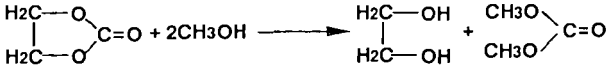
Y.Okada, T.Kondo, S.Asaoka, Chiyoda Corporation
3-13 Kanagawa-ku, Yokohama 221, Japan

Key wards : Dimethyl carbonate, Octane enhancing oxygenates, Zeolite catalysts

Abstract

We have taken note of the transesterification reaction as a highly safe process of dimethyl carbonate (DMC) production for fuel additives. The reaction proceeds under the low corrosiveness and in the relatively mild condition. We have aimed to use an inorganic solid catalyst for this process. The inorganic solid catalyst is thermally stable and can be used in the large-scale fixed bed reactors without a catalyst separation unit.

Through the transesterification of ethylene carbonate(EC) with methanol, DMC and ethylene glycol (EG) are co-generated as the products[1].



EG is one of the bulk chemicals produced in the large scale plant comparable to one for the fuel additives. The market balance is important in the co-production process. On the assumption that the amount of the co-production meets the market balance, the co-production of DMC and EG is commercially viable. If we can control the amount of the EG co-production in this process, it makes the process more flexible in the commercial production. Accordingly we have proposed a conceptual process scheme to control the amount of the EG co-production.

In this symposium, the inorganic solid catalyst system applying to the transesterification process and the conceptual process scheme how to control the amount of co-product will be discussed.

1.Introduction

Dimethyl carbonate (DMC) is very attractive as for use as an oxygenate for the fuel additives. Many routes of the DMC synthesis have been proposed. Among those routes, the DMC production process for the chemical raw material has been commercialized. The process for the fuel additives should be easy to scale up in the capacity to satisfy the large demand. Moreover, it is also required to be safe in the operation and to be stable in the supply.

2.Selection of DMC synthesis route

2-1 Probable routes of DMC synthesis

DMC is produced several ten thousands ton per year in the world as chemical raw material used in the carbonylating and methylating agent, etc. DMC had been formerly produced from phosgene. The proposed synthesis methods including commercialized routes as non-phosgene DMC production are classified generally into the following 4 routes. Fig.1 shows the relation of raw materials and intermediates of those routes. All routes start from methanol. There is the other route to produce DMC using nitrous acid ethers[2] except in Fig.1. This route has been in commercial for the chemical raw material use. Though the nitrous acid ethers are less toxic than phosgene, they are still considered as toxic materials. Accordingly, we put the process using nitrous acid ethers out of our research scope. The investigation results of the routes shown in Fig.1 are the following.

2-2 Oxidative carbonylation route

Oxidative carbonylation processes in both the liquid phase and the vapor phase have been developed. The liquid phase oxidative carbonylation is the oxidation of carbon monoxide with oxygen in methanol in the presence of copper chloride[3]. The catalyst is used in a slurry mixture. Now, DMC for the chemical use is being produced in this oxidative carbonylation process. In the vapor phase oxidative carbonylation, palladium chloride-copper chloride[4], cupric chloride on activated carbon[5], etc. is proposed as the catalyst. All of these oxidative carbonylation processes including technologies under development inevitably need the presence of both oxygen gas and chloride.

In these situation, Chiyoda Corporation has tried to investigate halogen-free solid catalysts to improve the oxidative carbonylation process in the view point of less corrosiveness and the separability of the catalyst. We have succeeded to find the zeolite fixed the cation of copper as this kind catalyst which is particularly effective as the catalyst of the following reactions.

$$2CuCl + 2CH_3OH + 1/2O_2 \longrightarrow 2Cu(OCH_3)Cl + H_2O$$

$$2Cu(OCH_3)Cl + CO \longrightarrow (CH_3O)_2CO + 2CuCl$$

2-3 Esterification route

The route from carbon dioxide and methanol into DMC through the dehydration is the simplest one. We have tried it challengingly. Since this reaction is very disadvantageous in the equilibrium, the reaction could not be successfully proceeded.

$$2CH_3OH + CO_2 \longrightarrow \begin{matrix} CH_3O \\ CH_3O \end{matrix}\!\!>\!C=O + H_2O$$

2-4 Route through urea

In this route, firstly urea is synthesized from carbon dioxide and ammonia. Subsequently, the urea reacts with methanol into DMC.

$$CO_2 + 2NH_3 \longrightarrow \begin{matrix} NH_2 \\ NH_2 \end{matrix}\!\!>\!C=O + H_2O$$

$$2CH_3OH + \begin{matrix} NH_2 \\ NH_2 \end{matrix}\!\!>\!C=O \longrightarrow \begin{matrix} CH_3O \\ CH_3O \end{matrix}\!\!>\!C=O + 2NH_3$$

Though methyl carbamate is easily generated as mono-changed intermediate in the second reaction step, the intermediate can not be transformed into DMC.

2-5 Transesterification route (glycol co-production route)

As shown in Fig.1, ethylene carbonate (EC) is used as the raw material instead of the direct reaction of carbon dioxide in the transesterification route. The EC is commercially produced from carbon dioxide and ethylene oxide. Subsequently, DMC is obtained from the EC through the transesterification with methanol. Ethylene glycol (EG) is converted from ethylene oxide as a main

co-product in this route. EG produced conventionally through the hydration of ethylene oxide is one of the bulk chemicals quantitatively comparable to fuel additives. In this transesterification route, the dried EG can be produced.

We have studied zeolite catalysts applying to the co-production of DMC and EG through the transesterification reaction. Zeolite catalysts have the excellent properties of resistance to heat and organic solvents and can be used in the large fixed bed reactors without a catalyst separation unit. We have found that some of zeolites have catalytic activity to the transesterifieation reaction. These results were presented at 207th ACS National Meeting. The catalytic activity depends on the Al_2O_3/SiO_2 ratio which represents the quantity of active sites. Since zeolite A has a maximum value of the Al_2O_3/SiO_2 ratio at 0.5 in the various type zeolites, the zeolite shows the highest activity. The cation species in the zeolite have an influence to the catalytic activity, the order of the activity is; 3A (KA) > 4A (NaA) > 5A (CaA).

2-6 Selection of the DMC synthesis route

Transesterification reaction is mild with small exotherm, and is carried out in the liquid phase without any toxic or corrosive chemicals. Therefore, it is essentially safe. Moreover, these features will be the merit in scaling up, because the large production will be able to perform with a low fixed capital.

In consideration of the above, we have selected the transesterification route as the most suitable one to large scale production of DMC for fuel additives and proceeded the further research in focus on this route.

3.The conceptual process of DMC production for fuel additives

3-1 The co-production of DMC and EG through the transesterification reaction

Fig.2 shows the conceptual process scheme of DMC production through the transesterification route. Fig.3 shows the concrete concept of the process scheme. The scheme consists of 9 units (blocks), ie. transesterification reactor, DMC-MeOH / EG-EC separation unit, MeOH separation unit, EC hydration reactor, etc. In the scheme, EG is co-produced quantitatively comparable to DMC.

3-2 The concept to control the EG co-production

If we can produce the only DMC or control the amount of the EG co-production in the selected route, it will make the process more flexible in the commercial production. This concept means that the large DMC production is possible freely from the demand of EG. Fig.4 shows the process scheme of the advanced concept. In this scheme, the co-produced EG is required to re-convert into the started EC. Accordingly, we have investigated the reaction to re-convert EG into EC.

In the first, we have conducted a test of the transesterification of EG and DMC, which is a reverse reaction of DMC and EG co-production. EC and methanol were generated with intermediate in stoichiometric proportions. It has been confirmed this transesterification is a reversible reaction. Therefore, we have considered EG would be able to re-convert into EC on the preferable catalyst. From the investigation of various reaction with the catalyst, we have confirmed that EC is generated from EG using urea instead of DMC.

3-3 The conceptual process of DMC production controlled the EG co-production

It is considered the combination of the EC regeneration reaction and urea synthesis makes the DMC production process controlled the EG co-production possible. Fig.5 shows the conceptual process scheme. In the scheme, urea is the intermediates synthesized from carbon dioxide and ammonia. Since the process of urea synthesis from carbon dioxide and ammonia had been established commercially, we can avail the process into the our proposed process complex without basic research. Fig.6 shows the total reaction scheme on which this conceptual process are based. In this reaction scheme, the DMC is synthesized from carbon dioxide and methanol through the dehydration reaction by the several steps.

4.Conclusion

we have selected the transesterification route as the most suitable one to large scale production of DMC for fuel additives. Transesterification reaction is mild with small exotherm, and is carried out in the liquid phase without any toxic or corrosive chemicals. Therefore, it is essentially safe. Moreover, these features will be the merit in scaling up. Zeolites can be used as the catalysts of this reaction. The zeolite catalysts have the excellent properties of resistance to heat and organic solvents and can be used in the fixed bed reactors without a catalyst separation unit.

EG is co-produced with DMC in the transesterification route. EG is one of the bulk chemicals quantitatively comparable to the fuel additives. On the assumption that the amount of the co-production meets the market balance, the co-production of DMC and EG is commercially viable.

As the option for this process, we have investigated the concept for the only DMC production or the control of the amount of the EG co-production. This concept means that the large DMC production is possible freely from the demand of EG. We have proposed the conceptual process scheme of the DMC production controlled the amount of the EG co-production. The conceptual process is consist of the urea synthesis and the re-conversion of EG into EC. In this conceptual process scheme, the DMC is synthesized from carbon dioxide and methanol through the dehydration reaction by the several steps. We have confirmed that EC is generated from EG using urea with the catalyst. However, the improvement of the catalyst and the investigation of the reaction conditions for the EC regeneration are required to rise the DMC yield in the total process.

5.References

1) John F.Knifton et al, J.of Molecular Catalysis, vol.67, 389-399 (1991)
2) EP 425197 (1990)
3) Ugo Romano et al., Ind. Eng. Chem. Prod. Dev., vol.19, 396-403 (1980)
4) EP 452997 (1988)
5) JP 91190846 (1991)

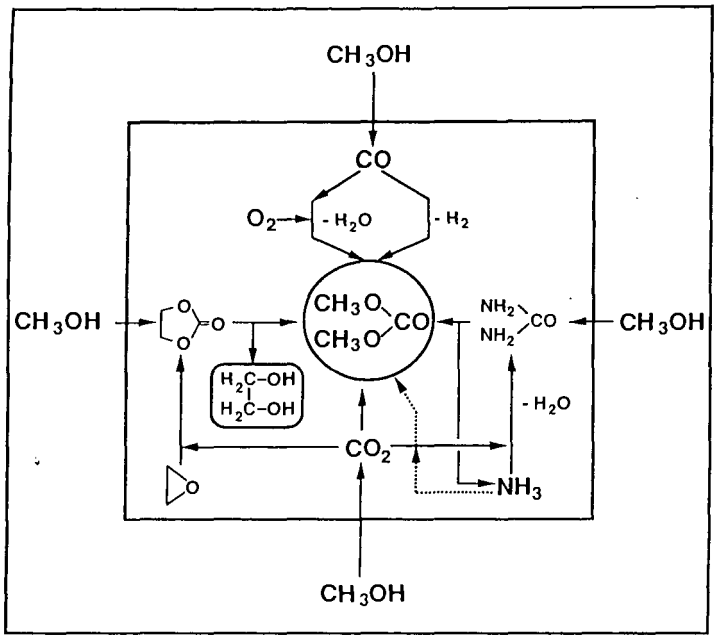


Fig.1 Routes of DMC synthesis without Cl_2CO

DMC:Dimethyl carbonate EC: Ethylene carbonate EG: Ethylene glycol

Fig.2 The conceptual process scheme of the DMC and EG co-production through the transesterification route

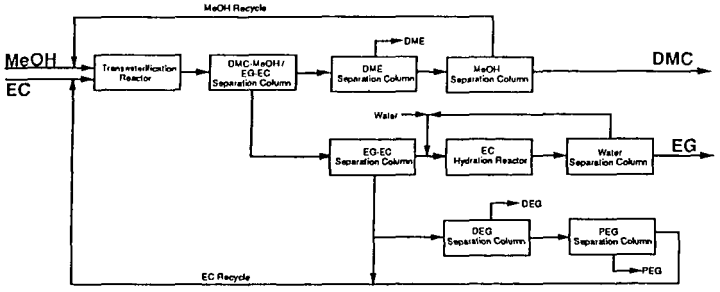
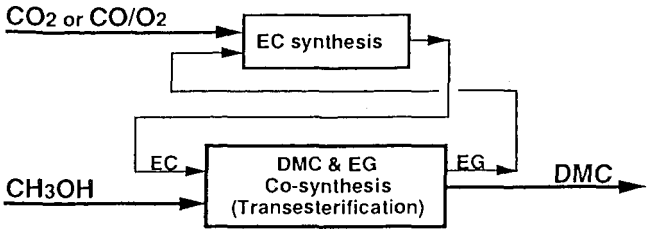
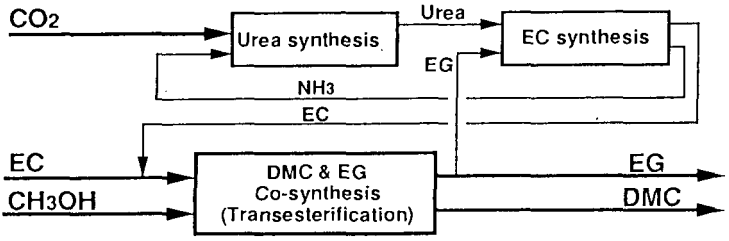


Fig.3 The concrete concept of the DMC and EG co-production process through the transesterification route



DMC:Dimethyl carbonate EC: Ethylene carbonate EG: Ethylene glycol

Fig.4 The conceptual process scheme of the DMC production without the EG co-production through the transesterification route



DMC:Dimethyl carbonate EC: Ethylene carbonate EG: Ethylene glycol

Fig.5 The conceptual process scheme to control the EG co-production in the DMC production through the transesterification route

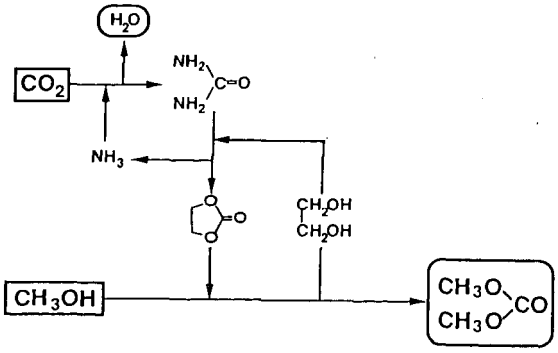


Fig.6 The reaction scheme of DMC synthesis from CH_3OH and CO_2

ISOBUTANOL SYNTHESIS FROM SYNGAS

C.-H. Finkeldei, B. Jaeger, W. Keim, K.A.N. Verkerk
Institut für Technische Chemie und Petrolchemie
RWTH Aachen, Worringerweg 1
52074 Aachen, Germany

Keywords: Isobutanol Synthesis, Synthesis Gas

INTRODUCTION

The hydrogenation of CO to oxygenates is a field of growing interest due to their properties as gasoline blends and the necessity to search for alternatives for future automotive fuels (1). While methanol synthesis from syngas is a well established process, the work on higher alcohol synthesis has been less successful. The demand for MTBE (Methyl-*tert*-butylether) is shifting the interest from higher linear alcohols towards the branched members, mainly isobutanol.

The application of slurry reactors for exothermic reactions has gained considerable interest in the industrial and academic world. For synthesis gas conversions the LPMeOH process by Air Products is a well known example (2). This prompted us to apply this technology to isobutanol synthesis which runs under more extreme reaction conditions.

Because of much easier and faster handling and the necessity to compare results from slurry reactions with the fixed bed reactions cited in literature fixed bed reactor systems are preferred for catalyst development and optimization. The main differences e.g. temperature gradients, backmixing and particle sizes will obviously have major influence on a reaction which mechanistically consists of a network from parallel and consecutive steps (3).

Due to this objective, a fixed bed reactor study has been performed running a typical isobutanol catalyst with different particle sizes and linear velocities. The catalyst developed by us consists of a potassium promoted ZrO_2/ZnO/MnO possessing high activity for isobutanol and methanol (4). These tests provide data to study the behaviour of residence time and temperature on reaction products. Furthermore mass transfer limitations which affect activity and selectivity (5) can be determined.

EXPERIMENTAL AND EQUIPMENT

The catalyst was prepared by coprecipitation of the metal nitrates with potassium hydroxide at 80 °C, keeping the pH constant at 11 ± 0.2. The precipitate was washed, pelletized and dried at 130 °C. After calcination at 450 °C for 3 hours (heating rate: 4°/min) the resulting catalyst was powdered, pressed and sieved to sizes of 0.25-0.50 mm and 1.60-2.0 mm.

For catalytic testing a continuous lab scale unit was set up which can be operated at temperatures up to 500°C and pressures up to 40 MPa. The unit was constructed to switch directly from fixed bed to slurry reactor. A Process management system and on line GC analysis with gas partitioner as well as an automatic product sampler for off line analysis allows continuous operation.

Catalyst activations and reactions have been carried out in a fixed bed reactor from stainless steel with an inner diameter of 9 mm. Catalyst particles have been mixed with an equal amount of copper particles of the same size. Glass particles were added on top as a preheating zone.

The catalyst was activated in situ by pressurizing with hydrogen (30 $Nl \cdot h^{-1}$, 3 MPa) and heated to 225 °C with a rate of 4°/min keeping this temperature constant for 120 min. Subsequently the reactor was pressurized with H_2/CO (1/:1) to 25 MPa while temperature was increased up to reaction conditions with 4°/min.

All reactions were conducted at 25 MPa varying temperature from 430 °C to 370 °C in steps of 30°. Afterwards the measurements at 430 °C were repeated to test reproducibility. At each temperature linear gas velocity was changed in six steps from 24 to 227 $Nl \cdot h^{-1}$. All setpoints were allowed to come to steady state for 75 min. Then the first on line measurement was started followed by collecting one off line sample. A second on line measurement 75 minutes later ended each analysis.

Using this procedure, four test runs have been performed changing bed volume from 2 ml to 4 ml of catalyst and particle sizes from 0.25-0.50 mm to 1.60-2.00 mm.

RESULTS AND DISCUSSION

Typical reaction conditions of the potassium promoted ZrO_2/ZnO/MnO catalysts are above 400 °C. Data to show yields of typical products from fixed bed reactions are given in Table 1. Runs up to 415 °C using a 300 ml CSTR with decalin as inert liquid proved the possibility to perform the isobutanol synthesis under slurry conditions. The advantage of removal of exothermic heat by an inert liquid is diminished by approaching the critical temperature. The differences in heat removal between decalin and the syngas itself become very small in high temperature reactions (6).

The fixed bed reactor study resulted that the CO conversion towards alcohols shows a clear dependence upon variation of particle size. All measurements show that activity increases with decreasing particle size which can be interpreted as mass transfer limitation by porous diffusion.
As presented in Figure 1, CO conversion to isobutanol is showing this behaviour in a typical way. Activity increases with increasing temperature following Arrhenius' law. The smaller particle sizes show higher conversions than the larger ones which is an effect of mass transfer limitation. The difference in activity between the two particle sizes grows with temperature due to the temperature dependence which is smaller for mass transfer than for chemical reaction kinetics.
The opposite behaviour can be observed in for the CO conversion to methanol (Figure 2). The activity decreases with temperature which can be explained through an approach to chemical equilibrium. At higher temperatures the values are close to equilibrium and no dependence on residence time can be seen. The measurement at 370 °C shows the characteristics discussed above reaching a steady state value at long residence times in the catalyst bed.
Film diffusion might be an additional limiting step in heterogeneously catalyzed reactions. The influence of film diffusion increases with temperature in the same way as porous diffusion and decreases with linear velocity by reducing laminary films covering the catalyst pellets. Figure 3 exhibits that film diffusion has no influence on CO conversion to isobutanol at 370 °C and only little effect at 430 °C.
The most accepted reaction network for higher alcohol synthesis given by Klier at al. for cesium promoted Cu/Zn-oxide catalysts describes the mechanistic differences between the reaction paths to methanol and isobutanol (3). The first step in higher alcohol synthesis is hydrogenation of CO to a surface intermediate which is very similar to methanol. Linear primary alcohols are built by linear chain growth including CO insertion steps. Isobutanol and 2-methylbutanol-1 origin from β-addition including aldolic condensation. Formation of 1-propanol can be reached via both pathways (Scheme 1).
Isobutanol and 2-methylbutanol-1 do not undergo consecutive reactions following this network. They cannot react further in aldolic condensations and the probability of linear chain growth is low. On the other hand the linear alcohols are able to undergo linear chain growth as well as β-addition.
The CO conversions to the afore mentioned alcohols ethanol, 1-propanol and 2-methylbutanol-1 are plotted in Figures 4, 5 and 6. The branched alcohol 2-methylbutanol-1 shows similarities to the conversion to isobutanol with an increasing activity with temperature (Figure 4). The conversions to ethanol (Figure 5) and 1-propanol (Figure 6) show a similar behaviour as described for methanol. They exhibit a lower activity at higher temperature and seem to be independent from linear gas velocity at 430 °C.

CONCLUSIONS

The fixed bed reactor study with the potassium promoted ZrO_2/ZnO/MnO catalyst proved that mass transfer limitations occur at high temperatures even with lab scale particle sizes of 1.60-2.0 mm. Further it could be shown that CO conversion to methanol follows an equilibrium behaviour at higher temperatures, whereas isobutanol does not. For the conversion towards linear alcohols a similar behaviour as observed for methanol was found, where 2-methylbutanol-1 follows the characteristics as pointed out for the other branched member isobutanol.
Future studies adress a further optimization of the ZrO_2/ZnO/MnO system in order to achieve milder reaction conditions which will benefit slurry reactor operations.

ACKNOWLEDGMENT

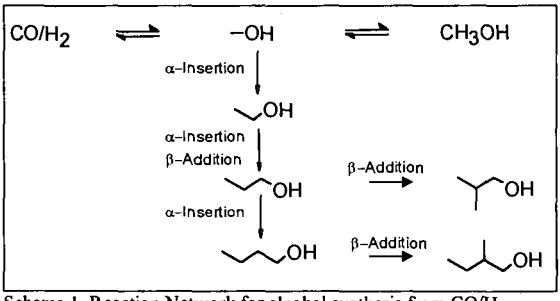
We thank the US Department of Energy and Air Products and Chemicals, Inc. for the support of this work.

LITERATURE

(1) R.R. Chianelli, J.E. Lyons, G.A. Mills, Catal.Today, 22, 361-396 (1994).
(2) G.W. Roberts, D.M. Brown, T.H. Huisung, J.J. Lewnard, Chem. Eng. Sci., 45(8), 2713-2720 (1990).
(3) K.J. Smith, C.-W. Young, R.G. Herman, K. Klier, Ind. Eng. Chem. Res., 30, 61-71 (1991).
(4) W. Falter, W. Keim, Catal. Lett., 3, 59-64 (1989).
(5) H. Berndt, V. Briehn, S. Evert, D. Gutschick, W. Kotowski, Catal. Lett., 14, 185-195 (1992).
(6) C.-H. Finkeldei, PhD Thesis (submitted), RWTH Aachen (1996).

T [°C]	370		430	
GHSV [h^{-1}]	12000	23250	12000	23250
STY [g/(l·h)]				
Methanol	478	748	242	516
Ethanol	37	43	17	30
1-Propanol	34	38	15	29
Isobutanol	34	35	176	265
2-Methylbutanol-1	11	12	19	29
U_{CO} [%]	25	16	48	42
S_{CO2} [%]	50	39	56	49

Table 1. Space time yields to alcohols with ZrO_2/ZnO/MnO/K catalyst in fixed bed reactor (V_{Cat} = 4 ml, Particle size: 0.25-0.50 mm)



Scheme 1. Reaction Network for alcohol synthesis from CO/H_2

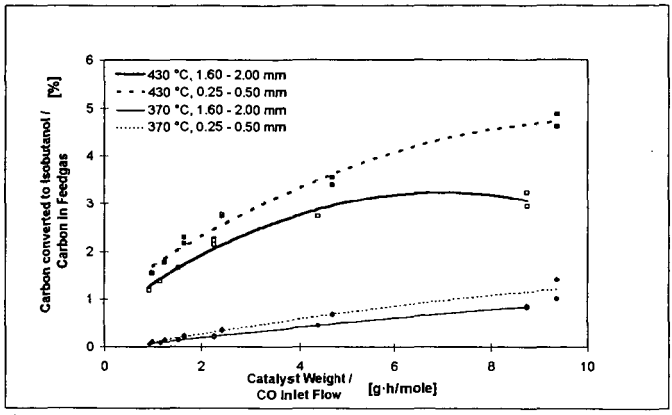


Figure 1. Effect of particle size on CO conversion to isobutanol (V_{Cat} = 4 ml)

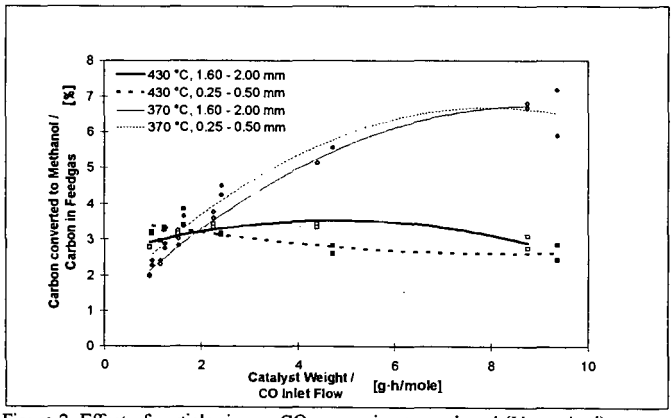


Figure 2. Effect of particle size on CO conversion to methanol (V_{Cat} = 4 ml)

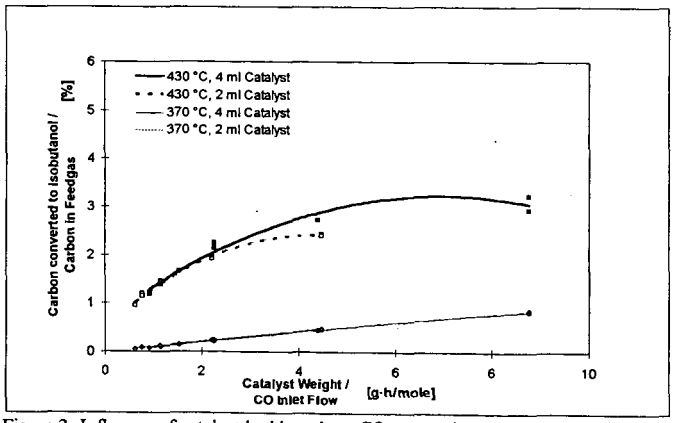


Figure 3. Influence of catalyst bed length on CO conversion to isobutanol (Particle Size: 1.60-2.00 mm)

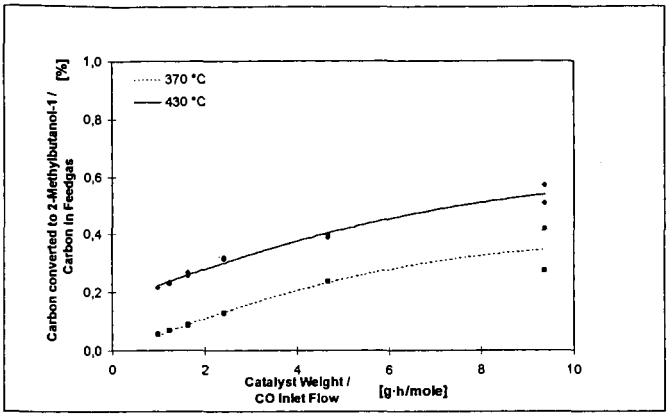


Figure 4. CO conversion to 2-methylbutanol-1 (V_{Cat} = 4 ml, Particle Size: 0.25-0.50 mm)

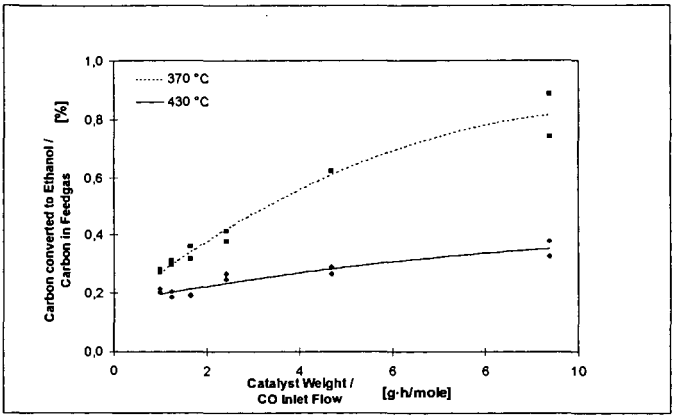


Figure 5. CO conversion to ethanol (V_{Cat} = 4 ml, Particle Size: 0.25-0.50 mm)

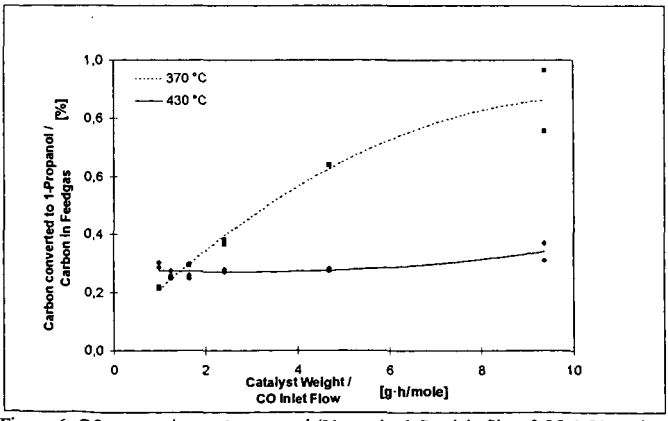


Figure 6. CO conversion to 1-propanol (V_{Cat} = 4 ml, Particle Size: 0.25-0.50 mm)

METHANOL vs ETHANOL -- '96

G. R. James, Paul T. Richards,
William E. Schaefer and Steven A. Wilmes
James Chemical Engineering, Inc.
110 South Road, Groton, Connecticut 06340

Keywords: Methanol, Ethanol, Manufacture

The objects of this paper are:

- To review the manufacture of ethanol and methanol.
- To compare current costs of manufacture.
- To look at current use situation.
- To comment on the current government subsidies for methanol and ethanol produced from renewable resources.
- To consider the possibilities of making methanol and ethanol from various renewable resources.

METHANOL

Methanol, known as "Wood Alcohol" for generations, was initially produced as a by-product from the destructive distillation of wood. Pyroligneous liquor, from heating wood in the absence of air, contains some 4 percent methanol and 7 percent acetic acid. Thus, wood produced the majority of methanol (and other by-products such as charcoal and fuel gas) until the mid 1920's.

Synthesis of methanol directly from H2 and CO appeared in the 1920's (in some cases methanol was a step in the purification of H2/N2 mixtures on route to ammonia synthesis). Methanol is still made directly from H2 and CO, which can be made from any hydrocarbon source. At present, natural gas is the major source, however, coal, oil, solid waste, and wood can and are being used to make methanol.

Methanol use (and price) have climbed, particularly in the past few years as shown in Figure #1. Figure #1 also illustrates that MTBE has been the significant driver of methanol demand in recent years.

The overall methanol market in the U.S. is expected to continue increasing by perhaps 10% in the next four years. At the same time, because of gas limitation in the U.S., imports are projected to increase from low priced gas locations with relatively low shipping costs to the U.S.

MTBE, the major driver in the past few years, has recently suffered some setback but is expected to continue growing at a moderate rate instead of the explosive rate of 1990 through 1995. The ETBE/Ethanol situation, briefly discussed below, has and will have considerable effect on the MTBE and methanol demand.

Federal Tax Credits in the past years for so-called renewable feed based fuel and gasoline additives (currently 54¢/gal. for ethanol and 60¢ for methanol) from 1978 raised production of ethanol from 800,000 short tons to 3,500,000 short tons by 1984. The credits or subsidies boosted the uneconomic use of corn based ethanol (food to fuel) but, unfortunately, did nothing for the biomass to methanol industry which makes considerable sense in the U.S. for several reasons:

1. Biomass* is available up to a large percent of our fuel use.
2. Methanol produces the most economical fuel oxygenate, MTBE.
3. Methanol itself is an efficient, clean burning fuel. As the biomass to fuel industry develops, it will compete with gasoline with no subsidy.

*Biomass includes:
- Solid waste
- Wood
- Agricultural residues (see Table 5)

ETHANOL

Known as "Grain Alcohol" for the millennia, ethanol has been the basis of recreational beverages forever. It can be made from fruit or sugar containing materials such as

molasses. For fuel use in the USA, it is made from starchy materials such as corn, barley and sorghum. These are all renewable resources and require, for example, about 0.38 bushel of corn per gallon of 100% ethanol. There are various by-products depending upon which system is used.

The "Wet Mill" system produces by-products such as germ, gluten and a small amount of CO2. The "Dry Mill" process produces DDGS (an animal feed supplement) and a small amount of CO2. There are disagreements in the industry as to which process is most economical. Apparently, it depends largely on the return from by-products at any particular time in the overall economy.

Ethanol is also made from petroleum sources by reaction of ethylene to ethyl sulfates and then hydrolysis to crude ethyl alcohol and dilute sulfuric acid (which is then concentrated for re-use). Another process produces ethanol directly from ethylene via hydration over a catalyst.

Subsidies to the ethanol industry have resulted in rapid changes in the past 15 years. Plant capacity in 1979 of only 20 MM gallons PA became 750 MM gallons PA in 1986 and in 1994 was some 1,400 MM gallons (renewable resource based). At the same time, because of variations in the cost of grain, raw materials (approximately 45% in 1994) and apparent reduction in demand (July 1994 data show 8% reduction in demand over 1993), many U.S. Government loan guaranteed ethanol plants have had difficulty.

The dramatic changes in ethanol demand in the USA over the last 30 years are illustrated in Figure #2.

In the recent pase two things have happened to the ethanol/fuel industry:

1. The corn price has gone up from $2.75 in August 1995 to a current price of $3.90/bushel. At .38 bushels per gallon, this equals some 38¢ per gallon net increase (see Figure 9).
2. The public is at last becoming aware of the give-away of public funds by both political parties to corporations using corn uneconomically to make ethanol.

PRODUCTION COSTS

Methanol

Although methanol can be produced from various raw materials, natural gas remains the major raw material for production of methanol as illustrated in Figure #3.

This, of course, is the result of lower capital and operating costs for natural gas based methanol production versus methanol produced from other feedstocks as shown in Figure #4.

The result is that locations with low cost natural gas are able to make methanol and ship it to markets. This provides a means of using remote natural gas and shipping it to market as methanol for low polluting direct fuel use or as a raw material for MTBE (36% methanol), the leading current gasoline additive.

If it were decided to make methanol from wood, then costs might be some $200/Ton or $80.00/Ton above the cost from natural gas (approximately 25¢ per gallon above natural gas cost). Given the government tax credit of 60¢ per gallon for methanol made from sources other than petroleum, natural gas or coal, production from wood may be a very attractive option.

Ethanol

Assume corn as the feed stock and other utilities as follows:

Steam	$6.00/2000 lb. ton
Power	$0.05/KWH
Corn	$2.25/bushel [now $3.90]
By-product Sales	65% of corn cost (Wet Mill)*
	50% of corn cost (Dry Mill)*

Depreciation, Taxes, Insurance and Maintenance = 18% PA

*Assume 50% increase in by-product return with $3.90/bushel corn.

Capital costs versus plant capacity are as given in Figure #5 for methanol plants based upon conventional reforming of natural gas, wet mill ethanol process plants, and dry mill ethanol process plants. Then production costs versus plant capacity are as given in Figure #6.

Thus, methanol can be made from natural gas ($2.00 /MM BTU Gas) versus ethanol from corn ($2.25/bushel) [$3.90/bushel] for approximate prices shown in Table 1.

However, if corn based ethanol receives 54¢ per gallon credit, in the $2.25/bushel corn it is somewhat less expensive than methanol per gallon. Also, since methanol has only 73% of the heating value of ethanol, ethanol should then win hands down as a direct fuel.

On the other hand, if renewable resourced methanol were used at 78¢ per gallon with a 60¢ per gallon credit, it would compete well with 98¢ ethanol (i.e. 78 - 60 = 18¢ methanol versus 98 - 54 = 44¢ ethanol). Also, methanol is 50% oxygen versus ethanol at 34.7%. Thus, if the water separation problem with direct methanol addition is solved with other additives, oxygen addition is easier with methanol.

Both the above paragraphs are considerably changed by the current $3.90 per bushel corn price. Thus, methanol without the tax credit is clearly ahead of ethanol on price at $3.90/bushel for corn with the tax credit (see Table 1 and Figure 9).

MTBE and ETBE

Major gasoline additives containing methanol and ethanol are MTBE (Methyl Tertiary Butyl Ether) and ETBE (Ethyl Tertiary Butyl Ether).

Table 2 shows the cost of production for MTBE based on:
1. approximate cost of methanol production at 50¢ per gallon
2. current methanol market price of $.45 per gallon
3. subsidized methanol price of $.78* - .60 (tax credit) = 18¢ per gallon

*Methanol from renewable resources (biomass)

The same table also shows the production cost of ETBE based on:
1. approximate cost of ethanol production at $1.10 per gallon [1.35]*
2. subsidized price of $1.10 [1.35] - .54 (tax credit) = 56¢ per gallon [81¢]

*[ ] = based on corn at $3.90/bushel

Figure #7 is a plot of estimated production costs of MTBE and ETBE versus plant capacity showing the variation of production costs with ethanol / methanol feedstock prices. It shows relative per ton costs of MTBE (36% Methanol) and ETBE (45% ethanol). It does not show the effect of oxygen content on RFG mixtures. Oxygen contents are as follows:

Ethanol	- 34.7%
MTBE	- 18.2%
ETBE	- 15.7%

Thus, for 2.0% and 2.7% oxygen mixtures the costs per gallon of RFG are shown in Table 3 for Ethanol, ETBE and MTBE.

In spite of the above figures, which show that ethanol is by far the most economical oxygenate of these three, particularly with the U.S. Government subsidy and other State benefits, and that ETBE (with the Tax Break) and MTBE are quite competitive, the published information to date shows that marketers are choosing MTBE by some 80% to 10% with another 10% undecided. There is some indication that ethanol may be in short supply, however, prices do not show as much variation in ethanol price as has occurred in methanol, for example. Thus, a more important consideration for ethanol may be the vapor pressure effects in summer and the problems with switching from one oxygenate to another as well as the question of who makes which material and whether blenders are concerned with cost of production or market price.

US Gulf Coast market prices for MTBE and Ethanol are illustrated in Figure #8.

ENERGY USE

A brief review of the cost of energy use in the manufacture of ethanol and methanol (see Table 4) indicates that per gallon of either energy costs are similar neglecting the energy required to make corn fed into the ethanol process.

While manufacture of methanol from natural gas seems to use the least energy, methanol from wood (including the wood), costs only 40% more for energy than the dry mill ethanol system (excluding the cost of corn).

Figures prepared by the U.S. Dept. of Energy indicate that some 40 quadrillion BTU/year can be available through wood utilization in our forests. Another 4.2 quads is available from forest residues. Of this, the Department of Energy estimates that 6 quads can be captured. Other agricultural residues and municipal solid waste add up to some 4 quads for a total of some 10 quads that can be converted to ethanol or methanol.

Table 5 shows the estimated production of ethanol or methanol from these materials. The projected amounts are 54 x 10^9 gallons of ETOH in the year 2000 or 154.7 x 10^9 gallons of MEOH in the year 2000 - (equals 8.7 quads of energy). Total energy use in the U.S. in 1992 has been estimated at 82 quads.

CONCLUSIONS

1. Methanol can be made for about half the cost of ethanol per gallon.
2. More methanol than ethanol (about 3 times as much) can be made from renewable raw materials available.
3. Subsidies and loan guarantees to ethanol producers have benefited a few but by and large they have not brought about a strong ethanol based fuel sector. (Note the upset in ethanol caused by the high price of corn this year.)
4. It appears that encouraging ethanol production from corn over methanol from natural gas actually results in use of more fossil fuel for energy than if the energy were used directly. Further, it appears that methanol from wood using 16¢ worth of power per gallon will consume less fossil fuel energy than ethanol from corn (20¢/gal., excluding the energy used in growing the corn).
5. The current tax subsidy for renewable resource based methanol and MTBE, the use of wood as a feedstock may be an attractive option.
6. Use of corn to make fuel seems to be a waste. Corn is a food. It could be used to feed people in areas of the world suffering from lack of basic food.

LITERATURE CITED

1. Wood, P.R., "New ETOH Process Technology Reduces Capital and Operating Costs for Ethanol Producing Facilities", PSI, Memphis TN, *Fuel Reformulation*, July/August 1993.
2. James, G.R., P.T. Richards and W.E. Schaefer, "MEOH From Gas, Coal or Residual Oil", presented at the Asian Methanol Conference, Singapore, (1993).
3. James, G.R., B.L. Huson and P.T. Richards, "MEOH and MTBE - Their Relationships in Manufacturing and Marketing", presented at The Fertilizer Association of Indonesia Conference (APPI) (1991).
4. "21st Century Fuel News", Hart Publications, November 1994 and "Oxy Fuel News", Hart Publications, October 1994.
5. "21st Century Fuels", Hart Publications, May & June 1994, February & April 1996.
6. Kane, S. and J. Reilly, "Economics of ETOH Production in the U.S.", U.S. Dept. of Agriculture Economic Report #607, March 1989.
7. Candella, J.P., "Fuel Ethanol: Profit Margins and Product Flexibility for the Gasoline Marketer", presented at the National Conference on Fuel Ethanol, Washington, D.C. (1988).
8. U.S. Department of Energy Fact Book, 1980.
9. "Corn Fertilizer Information", Fertilizer Round Table, Atlanta, GA, 1982.
10. Unzelman, George, "U.S. Gasoline Composition: '90 Decade and Horizons", *Fuel Reformulation*, May/June 1994.
11. Singh, Margaret and Barry McNutt, "Energy and Oil Input for Producing Reformulated Gasolines", *Fuel Reformulation*, Sept./Oct. 1993.
12. Haigwood, Burl, "September/October Fuel Reformulation MTBE Survey", *Fuel Reformulation*, Sept/Oct. 1993.

13.Office of Highway Information Management; Highway Funding and Motor Fuels Division "Highway Taxes and Fees", May 1995.
14.Federal Register Vol. 60 No. 151 Rules and Regulations, August 1995.
15.Chas. A. Stokes, Sc.D, P.E., "The Methanol Industries Missed Opportunities", 1995 World MEOH Conference, Phoenix, Arizona
16.Albert J. Smith, III, Chas. A. Stokes and Peter Wilkes, "The Rebirth of Methanol From Biomas", World MEOH Conference, Atlanta, GA, November 29 - December 1, 1993.
17.Refining Economics Report, February 1996.
18.Hart's "Octane Week", April 29, 1996, Vol. XI, No. 18.

TABLE 1 CORN AT $2.25 / BUSHEL				
CAPACITY	METHANOL ¢/GAL.	ETHANOL ¢/GAL.		AVERAGE DELTA ¢
		WET MILL	DRY MILL	
500 STD	64.50	[135.00] 100.00	[140.00] 99.00	[73.00] 35.00
1000 STD	53.25	[126.00] 91.00	[133.00] 92.00	[76.20] 38.30
1500 STD	48.61	[122.00] 87.00	[130.00] 89.00	[77.40] 43.40
[@ $3.90/bushel. Includes 50% increase in by-product sales price]				

TABLE 2 MTBE and ETBE PRODUCTION COST					
				MTBE	ETBE
	PLANT CAPACITY (STD)			607	704
	Units	Unit Price	Unit Cons.	Annual Cost (1000's)	Annual Cost (1000's)
RAW MATERIALS					
Isobutylene for MTBE	Ton	$200	0.64	$25,640	
Isobutylene for ETBE	Ton	$200	0.55		$25,555
Methanol	Ton		0.364	see below	
Ethanol	Ton		0.45		see below
Catalyst	Ton	$4,550	0.00018	$164	$190
UTILITIES					
Steam	Lb	$0.006	1,000	$1,202	$1,394
Power	kwh	$0.05		$80	$93
Cooling Water	1000 gal	$0.113		$97	$113
LABOR					
Operating	MH	20.00	24,000	$480	$480
Overhead (150%)				$720	$720
REPAIR & MAINTENANCE				$698	$768
LABORATORY, SUPPLIES, & MISC.				$175	$175
TOTAL OPERATING COST				$29,256	$29,488
INTEREST (10% Debt)				$1,396	$1,536
TAXES & INSUR. (2%)				$465	$512
DEPRECIATION				$2,327	$2,560
NET PRODUCTION COST WITHOUT MEOH/ETOH				$33,445	$34,095
PRODUCTION COST / ST MTBE WITHOUT MEOH				$166.96	
PRODUCTION COST / ST ETBE WITHOUT ETOH					$146.76
PROD. COST / ST MTBE - MEOH AT $0.50 / GAL.				$221.56	
PROD. COST / ST MTBE - MEOH AT $0.45 / GAL.				$216.10	
PROD. COST / ST MTBE - MEOH AT $0.18 / GAL. (.78-.60)				$186.62	
PROD. COST / ST ETBE - ETOH AT $0.95 / GAL. [at 1.35/gal]					$276.11 [330.57]
PROD. COST / ST ETBE - ETOH AT $0.39 / GAL. (with $0.54/gal Tax Subsidy) [$0.81/gal.]					$199.86 [257.05]

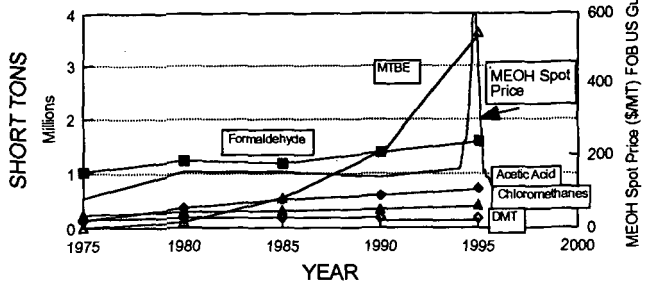
TABLE 3 CORN AT $2.25/BUSHEL		
	2% ¢/Gal.	2.7% ¢/Gal.
Ethanol - Wet Milled	[7.25] 5.24	7.08
(TB)	[4.15] (3.23)	(4.36)
Dry Milled	[7.66] 5.30	7.16
(TB)	[4.55] (3.28)	(4.44)
ETBE - (ETOH Cost)	[14.04] 11.75	15.86
(ETOH, TB)	[10.92] (8.49)	(11.46)
MTBE - (MEOH Cost)	8.12	10.95
(MEOH/TB)	(6.84)	(9.23)
TB = With Tax Break [ ] = Corn at $3.90/bushel		

TABLE 4 ENERGY COST PER GALLON OF PRODUCT			
	$/GAL.		NET CORN COSTS
Ethanol Wet Mill Steam & Power Dry Mill Steam & Power	 0.24* 0.20*	*Neglects corn use and energy required to produce it.	 30¢/gal. [52] 45.5¢/gal. [79]
Methanol From Natural Gas Natural Gas & Power From Wood	 0.186** (.178 from gas) 0.28** (.12 from wood)	**Includes Natural Gas at $2.00/MM BTU and wood at $20.00/ Ton	
[ ] = corn at $3.90/bushel			

TABLE 5 Projected Maximum Alcohol Production from U.S. Biomass Resources (Source: U.S. Department of Energy)								
	(Billions of Gallons/Year)							
	1980		1985		1990		2000	
	ETOH	MEOH	ETOH	MEOH	ETOH	MEOH	ETOH	MEOH
Wood	23.5	86.3	21.8	80.2	20.2	74.2	25.8	95.0
Agricultural residues	9.1	33.4	10.3	38.1	11.3	41.5	13.1	48.1
Grains								
Corn	2.3		2.1		0.9			
Wheat	1.2		1.4		1.6		2.0	
Grain Sorghum	0.4		0.3		0.3		0.3	
Total Grains	3.9		3.8		2.8		2.3	
Sugars								
Cane			0.2		0.7		0.7	
Sweet Sorghum			0.2		3.0		8.3	
Total Sugars			0.4		3.7		9.0	
MSW	2.2	8.6	2.3	9.2	2.5	9.9	2.9	11.6
Food Processing Waste								
Citrus	0.2		0.2		0.3		0.4	
Cheese	0.1		0.1		0.1		0.2	
All Other	0.2		0.3		0.3		0.3	
Total Processing Waste	0.5		0.6		0.7		0.9	
TOTAL	39.2	128.3	39.2	127.5	41.2	125.6	54.0	154.7
Based on following biomass-alcohol conversion factors: Wood and agric. residues-173 gal methanol per dry ton, 47 gal ethanol per dry ton. Corn-2.6gal ethanol per bushel. Wheat-2.7 gal ethanol per bushel. Grain sorghum-2.6 gal ethanol per bushel. Sugars-136 gal ethanol per ton fermentable sugars. MSW-100 gal methanol per dry ton, 25 gal ethanol per dry ton. Citrus waste-107 gal ethanol per dry ton. Cheese waste-95 gal ethanol per dry ton. Other food processing waste-90 gal ethanol per dry ton.								

Figure #1: US METHANOL CONSUMPTION

By End Products



Methanol consumption from other markets range from 0.82 - 1.35 MM short tons Per Year
Total methanol consumption in the US in 1995 approximately 8 MM short tons

Figure #2: US ETHANOL CONSUMPTION

By End Product

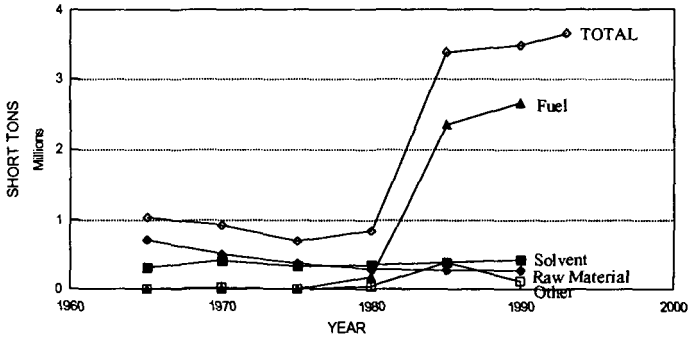
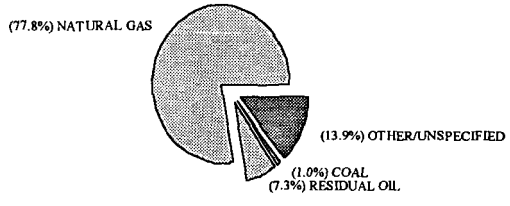


Figure 3: WORLD METHANOL PRODUCTION

BREAKDOWN BY FEEDSTOCK



Source: Various

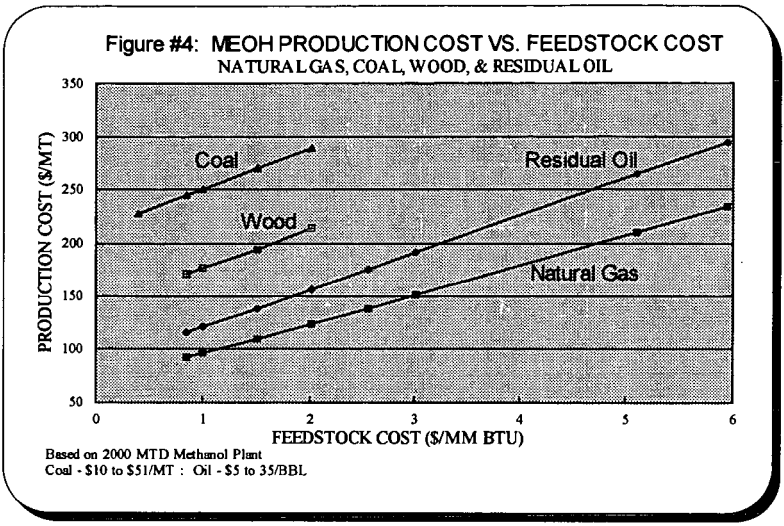


Figure #4: MEOH PRODUCTION COST VS. FEEDSTOCK COST
NATURAL GAS, COAL, WOOD, & RESIDUAL OIL
PRODUCTION COST ($/MT)
350
300
250
200
150
100
50
Coal
Residual Oil
Wood
Natural Gas
0
1
2
3
4
5
6
FEEDSTOCK COST ($/MM BTU)
Based on 2000 MTD Methanol Plant
Coal - $10 to $51/MT : Oil - $5 to 35/BBL

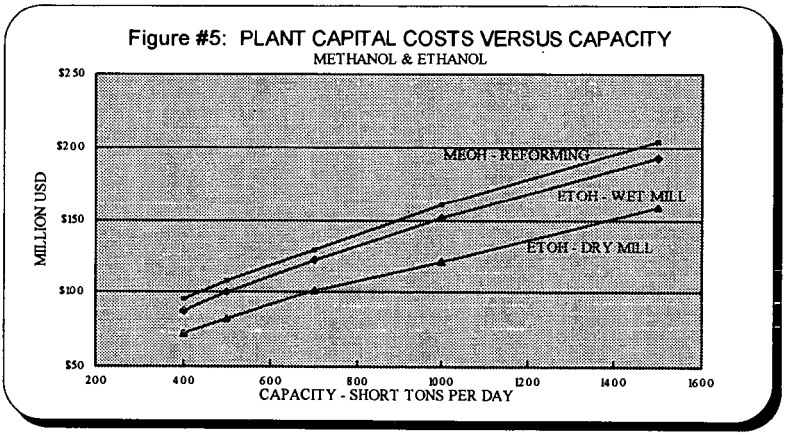


Figure #5: PLANT CAPITAL COSTS VERSUS CAPACITY
METHANOL & ETHANOL
MILLION USD
$250
$200
$150
$100
$50
MEOH - REFORMING
ETOH - WET MILL
ETOH - DRY MILL
200
400
600
800
1000
1200
1400
1600
CAPACITY - SHORT TONS PER DAY

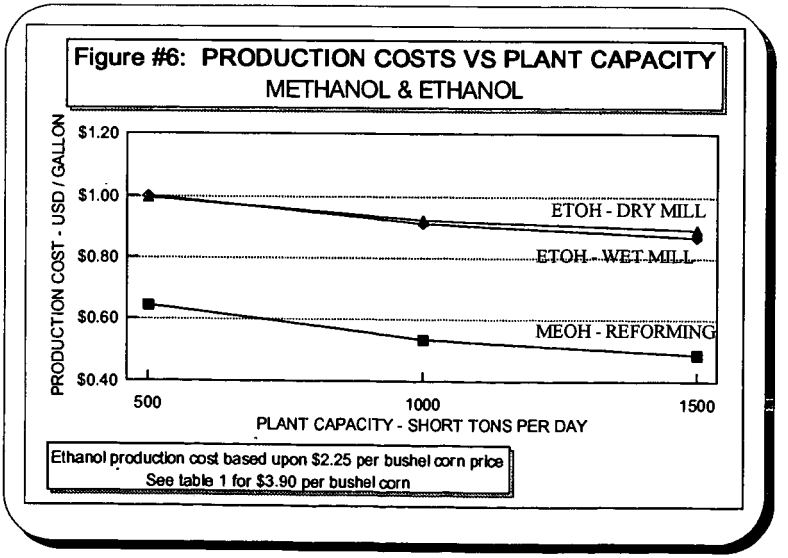


Figure #6: PRODUCTION COSTS VS PLANT CAPACITY
METHANOL & ETHANOL
PRODUCTION COST - USD / GALLON
$1.20
$1.00
$0.80
$0.60
$0.40
ETOH - DRY MILL
ETOH - WET MILL
MEOH - REFORMING
500
1000
1500
PLANT CAPACITY - SHORT TONS PER DAY
Ethanol production cost based upon $2.25 per bushel corn price
See table 1 for $3.90 per bushel corn

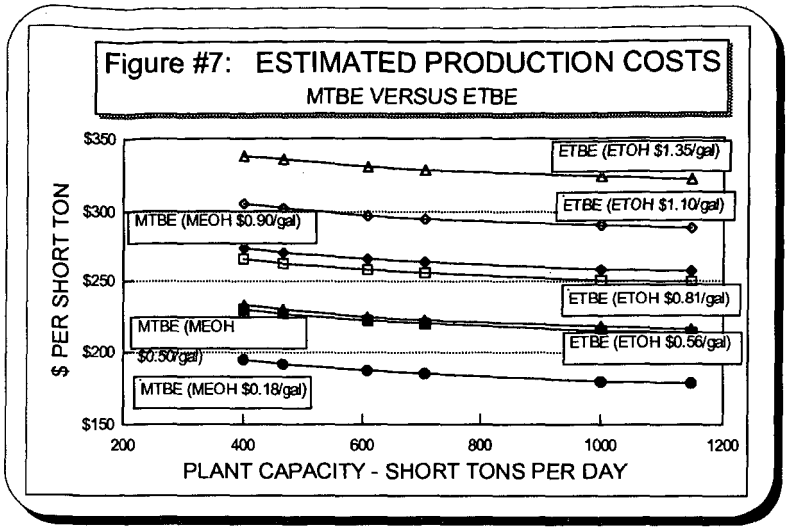


Figure #7: ESTIMATED PRODUCTION COSTS
MTBE VERSUS ETBE
$ PER SHORT TON
$350
$300
$250
$200
$150
200
400
600
800
1000
1200
PLANT CAPACITY - SHORT TONS PER DAY
ETBE (ETOH $1.35/gal)
ETBE (ETOH $1.10/gal)
MTBE (MEOH $0.90/gal)
ETBE (ETOH $0.81/gal)
MTBE (MEOH
$0.50/gal)
ETBE (ETOH $0.56/gal)
MTBE (MEOH $0.18/gal)

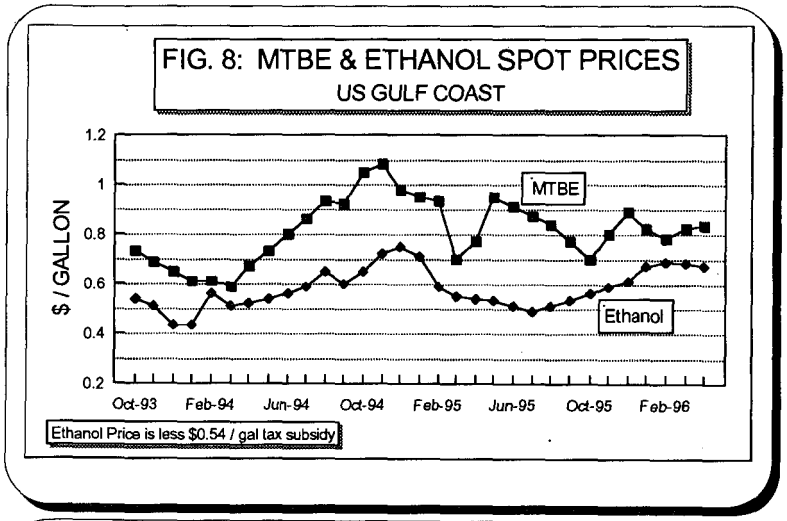


FIG. 8: MTBE & ETHANOL SPOT PRICES
US GULF COAST
$ / GALLON
1.2
1
0.8
0.6
0.4
0.2
Oct-93
Feb-94
Jun-94
Oct-94
Feb-95
Jun-95
Oct-95
Feb-96
MTBE
Ethanol
Ethanol Price is less $0.54 / gal tax subsidy

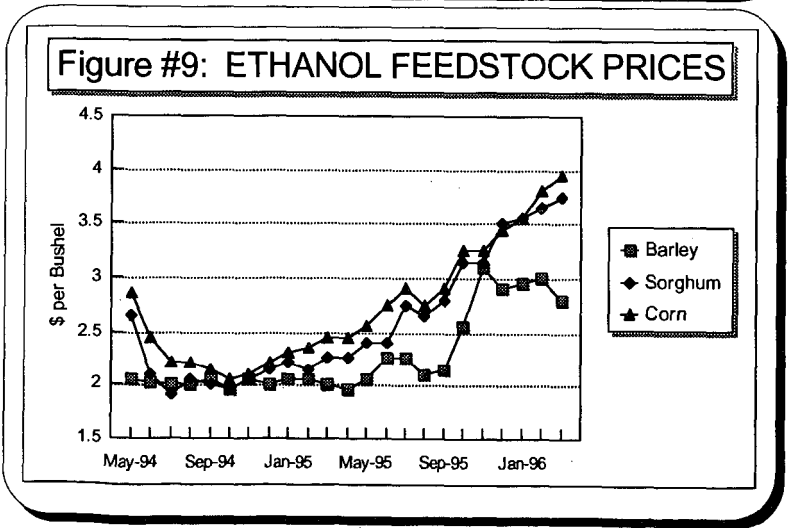


Figure #9: ETHANOL FEEDSTOCK PRICES
$ per Bushel
4.5
4
3.5
3
2.5
2
1.5
May-94
Sep-94
Jan-95
May-95
Sep-95
Jan-96
Barley
Sorghum
Corn

Maximizing the FCC's Potential for RFG Production

Lark E. Chapin
Stone & Webster Engineering Corporation
1430 Enclave Parkway
Houston, TX 77077

Keywords: Propylene, Catalytic Cracking , RFG

INTRODUCTION

The Fluidized Catalytic Cracking (FCC) unit has traditionally been the dominant conversion process in U.S. refineries. It has served as a major source of high octane naphtha for blending into the gasoline pool. With the passage of the Clean Air Act, U.S. refiners are reformulating their gasoline blends utilizing increasing volumes of "clean burning" alkylate and ethers. Both of these premium products use light olefins including propylene as feedstocks. Environmental trends in other major world markets will force much of the world FCC operating capacity to follow the same path.

Concurrently, the petrochemical demand for light olefins, in particular propylene, has outpaced conventional supply routes (ie., steam crackers). Propylene production from steam cracking is highly dependent on the overall economics for ethylene production. Given the current and anticipated demand for propylene relative to ethylene and the fact that the Steam Cracker can not offer the necessary flexibility to modify yields, it is likely that refinery sourced propylene will grow in importance. Obviously, a need for an economical light olefin generating process is required to meet the demand of these light olefins. New catalytic cracking technologies, such as Deep Catalytic Cracking(DCC), appear to be very promising for this application.

DCC is a new commercially proven fluidized catalytic cracking process for selectively cracking a wide variety of feedstocks to light olefins. The technology was originally developed by the Research Institute of Petroleum Processing (RIPP) and Sinopec both located in the Peoples Republic of China. Stone & Webster is the exclusive licensor of this technology outside of China. Currently three units are operating in China and another three are under construction. One of the units under construction is part of a Stone & Webster grassroots DCC complex in Thailand for Thai Petrochemical Industry Co. Ltd.

Although DCC can readily be integrated into either a refinery or petrochemical facility, the intent of this paper is to quantify its impact on the gasoline pool and overall profitability of a U.S. Gulf Coast refinery dedicated to making reformulated gasoline (RFG).

PROCESS DESCRIPTION

DCC is a fluidized catalytic process for selectively cracking a wide variety of feedstocks to light olefins. Propylene yields over 20 wt% are achievable with paraffinic VGO feeds. A traditional reactor/regenerator unit design is employed using a catalyst with physical properties similar to traditional FCC catalyst. The DCC unit may be operated in one of two operational modes: Maximum Propylene (TYPE I) or Maximum Iso-Olefins (TYPE II). Each operational mode utilizes an unique catalyst as well as reaction conditions. DCC Maximum Propylene (Type I) uses both riser and bed cracking at severe reactor conditions while Type II utilizes only riser cracking like a modern FCC unit at milder conditions.

The overall flow scheme of DCC is very similar to that of a conventional FCC. However, innovations in the areas of catalyst development, process variable selection, and severtiy enables the DCC to produce significantly more olefins than FCC. A detailed process description has been published previously[1] and is not included in this paper.

DCC PRODUCT YIELDS

DCC reaction products are light olefins, high octane gasoline, light cycle oil, dry gas and coke. Typical Type I and II DCC yields are shown in the Table 1. Yields for FCC in a maximum olefin operating mode with a low rare earth , high mesopore activity, and high ZSM-5 catalyst are shown for comparison.

Table I
DCC vs. FCC Yield Comparison, wt%

Products	DCC Type I	DCC Type II	FCC
Dry Gas	10.9	5.6	3.2
LPG	41.0	34.2	31.8
Naphtha	26.6	39.2	34.6
LCO/HCO	12.7	15.9	25.2
Coke	8.8	4.6	5.2
Total	100.0	100.0	100.0
Ethylene	6.1	2.3	0.9
Propylene	20.5	14.3	11.4
Butylene	14.3	14.6	11.2
in which $IC_4^=$	5.4	6.1	4.2
Amylene	--	9.8	8.5
in which $IC_5^=$	--	6.5	4.3

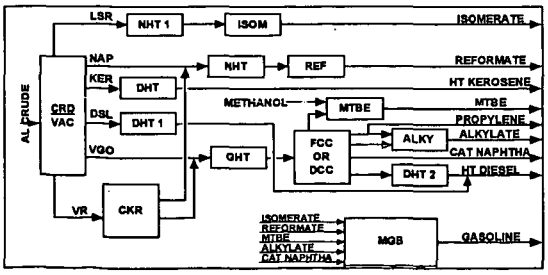
Although large amounts of dry gas are produced in the DCC Type I operation it is rich in ethylene and may be desirable for petrochemical enduse. Propylene is abundant in the DCC LPG stream and considerably higher than FCC. The DCC LPG is also rich in butylenes making it an ideal MTBE and/or alkylation feedstock. Of particular interest is the selectivity of both Type I and II towards $IC_4^=$. The ratio of isobutylene to total butylene is much higher for DCC than FCC(38-42 vs. 17-33 wt%). The same result is true for the isoamylene to total amylene ratio. Obviously , this can have a significant impact on downstream MTBE and TAME production capabilities. The high olefin yields are achieved by seleetively overcracking naphtha.

Because of the high conversion, all of the DCC C_5+ liquid products are highly aromatic. Consequently the octane values of the naphtha are quite high: 84.7 MON and 99.3 RON . The BTX content of the naphtha is over 25 wt % making it suitable for extraction. The naphtha will need to be selectively hydrotreated to improve its stability due to the di-olefin content. This is easily accomplished without octane loss.

The LCO will need further upgrading before it can be included in the diesel pool or it can be used as an excellent cutter stock due to its low viscosity and pour point. The HCO and small amounts of slurry oil can go directly to fuel oil blending or be used as hydrocracker feedstock.

CASE STUDY BASIS

In order to illustrate the overall economic impact of adding either DCC Type I or II versus an FCC in a U.S. Gulf Coast refinery dedicated to the production of reformulated gasoline three possible processing options were examined. Each case was analyzed with regard to the disposition of propylene (ie., alkylation or petrochemical sales). An overall onstream factor of 94 % was used for the 100,000 BPD refinery. The production rate was optimized based on producing prime fuels and fuel grade coke from an Arabian Light Crude source. Wright-Killen's 'Refine" model was used to evaluate the different processing scenarios. A simplified overall Block Flow Diagram is shown above.



Purchased feedstocks included butanes, methanol and MTBE. The primary products were:

- LPG(C_3/ C_4's)
- Reformulated Gasoline
- Jet/ Low Sulfur Diesel
- Fuel Grade Coke
- Sulfur

The feedstock and product prices are reported in Table 5 which can be found at the end of the paper. These prices represent typical current U.S. Gulf Coast Basis. Product specifications used to constrain the model are reported in Table 6. Key gasoline blending parameters were set so that the resulting reformulated gasoline pool would :

- Not exceed 1 LV% Benzene
- Contain 2 Wt% Oxygen, and
  Meet EPA mandated reductions in emissions

A simple economic evaluation was performed utilizing the following assumptions:

Delta Capital Cost:	Estimated for U.S. Gulf Coast
Project Life:	20 years from completion
Depreciation:	10 years straight line
Salvage Value:	20% of original investment
Tax Rate:	35% starting in year 1
Inflation Rate:	0 %
Feedstock Prices:	Constant based on current U.S. Gulf Coast prices
Product Prices:	Constant based on current U.S. Gulf Coast prices
Delta Utility Cost:	Constant current average prices
Operating Capital:	0
Investment Timing:	All in year 0

The price of propylene was varied from +/- 30% of the base cost to determine the sensitivity to propylene cost.

RESULTS

The following tables summarize the gasoline pool quality, operating severities, revenues,and overall economics for each case. As previously mentioned the price of propylene was varied to determine its impact for the cases where propylene is routed to sales and is shown in Figure 1 later in the paper.

The impact of switching propylene from petrochemical sales to alkylation and ultimately to the gasoline pool is readily apparent in each case. as shown in Table 2. The DCC operation magnifies this effect over the FCC operation. DCC Type I produces the largest amount of propylene and the least amount of gasoline. The isobutane requirment for the cases where the propylene goes to alkylation is quite substantial for the DCC options. In addition, the increased isobutylene yield with both DCC Type I & II significantly reduces the purchased

Table 2
Feedstocks and Products

Feedstocks, BPD	**Base Case FCC**		**Case 1 DCC I**		**Case 2 DCC II**	
C3= Disposition	**Alky**	**Sales**	**Alky**	**Sales**	**Alky**	**Sales**
Crude	100,000 BPD		100,000 BPD		100,000 BPD	
Isobutane	4684	1174	14433	1705	11831	2162
Methanol	342	342	914	914	1042	1042
Purchased MTBE	6105	5533	5041	2972	4755	3184
Products, BPD						
Propylene		2722		9860		7491
LPG (C3 & C4)	4345	4345	5603	5603	6190	6190
Gasoline (RFG)	63716	58240	70462	50625	70940	55869
Low Sulfur Diesel	24712	24712	21615	21615	21220	21220
Jet Fuel	14621	14621	14621	14621	14621	14621
Coke (Ton /day)	820	820	817	817	815	815
Sulfur (Lton/day)	203	203	203	203	203	203
Refinery Fuel (FOEB)	1985	1985	4846	4846	2532	2532

MTBE requirement.. The LPG make also increases significantly with both types of DCC operation. The middle distillate production is relatively constant for each case.

The operating severities for each unit are shown in Table 3. The reformer severity was kept constant for all cases at 97 RON. Although a future case might be warranted where the severity is lowered. The reformer feed was prefractionated to an IBP of 190°F to minimize the benezene precursors. The DCC has a much higher C5+ liquid conversion than the FCC.

Table 3
Operating Severities

Qualities	Base Case FCC		Case 1 DCC I		Case 2 DCC II	
C3= Disposition	Alky	Sales	Alky	Sales	Alky	Sales
FCC/DCC Conversion, vol%	75.8	75.8	85.3	85.3	86.8	86.8
Reformate, RON	97	97	97	97	97	97
Captive MTBE, BPD	1004	1004	2679	2679	3056	3056
Purchased MTBE, BPD	6105	5533	5041	2972	4755	3184

The gasoline pool was constrained to meet Federal Phase 1 RFG specifications and if possible CARB specifications. The purchase of MTBE was limited to a maximum of 2.0 wt% for all cases. The Rvp requirement of 7.1 applies only in the summer months and can be quite difficult to meet. Although pulling all of the normal butane from the pool may seem like the obvious first step it is often not desirable as addition of this blendstock permits the refiner an easy control of his pool Rvp. Alkylating the propylene versus selling it satisfies the more stringent summer Rvp requirement in all cases. The alkylate dilutes the overall pool with its low Rvp. The dilution effect of the alkylate is also evidenced by the reduction in aromatics, olefin and sulfur content of the pool as compared to the cases where the propylene is sold.

Table 4
Gasoline Pool Quality

Qualities	Base Case FCC		Case 1 DCC I		Case 2 DCC 2	
C3= Disposition	Alky	Sales	Alky	Sales	Alky	Sales
RON	95.7	95.7	96.7	97.4	96.3	96.6
MON	86.9	86.4	89.0	87.8	88.5	87.5
FON	91.3	91.1	92.9	92.6	92.4	92.1
RVP	7.1	7.2	6.8	7.2	6.8	7.2
Olefin, vol%	7.9	8.7	6.6	9.2	7.4	9.3
Aromatics, vol%	24.2	26.5	21.9	30.6	22.5	28.6
Benzene, vol%	0.86	0.95	0.63	0.87	0.69	0.88
Oxygen, wt%	2.0	2.0	2.0	2.0	2.0	2.0
Sulfur, ppmw	32	35	34	46	46	57

Does not meet one of the following Federal Phase 1 specifications : 7.1 RVP max 9.1 vol% olefins or 27 vol% aromatics.

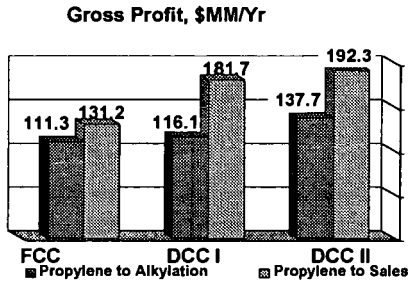
Although the aromatic, olefin and Rvp Phase 1 RFG specifications are not met in Cases 1 and 2 where the propylene is sold the reformer severity can be lowered bringing these specifications easily into compliance. For example, when the reformer severity is lowered to 89 and 92 for Cases 1 & 2 respectively the pool specifications are met. The FON drops to 89.5 and 90.0 for Case 1 and Case 2 at these severities.

The T50 and T90 specifications were not evaluated for this study as the 'Refine" model does not accurately account for changes in product distillations. Typically, the T90 specification is one of the most difficult and costly specifications to meet. Complying with this specification will also have a great impact on reducing the T50. FCC gasoline and reformate typically do

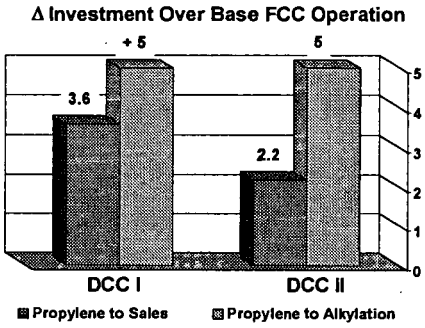
not meet the T90 specification and will require further fractionation or processing. This evaluation is outside the scope of this study basis.

ECONOMIC ANALYSIS

The gross profit for each case is shown in the following bar chart. For the cases where propylene is routed to alkylation, both DCC type I and II generate more gross profit than the FCC case. DCC type II is the most favorable option. The gross profit for the cases where propylene is routed to petrochemical sales shows that both DCC Type I and II are more profitable than the base FCC operation. Of the DCC operations, DCC type II again generates the greatest gross profit.



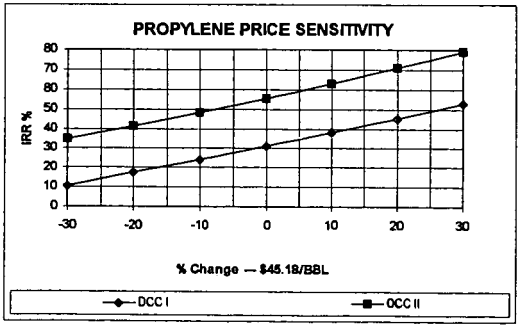
The Internal Rate of Return (IRR), Payout and Net Present Value figures were calculated for the cases where propylene was routed to alkylation or to sales for each type of operation. The analysis showed that for the cases where propylene was routed to alkylation the DCC Type II operation was the most profitable with an IRR of 20.3%. The cases where propylene was routed to petrochemical sales showed that the installation of an DCC unit in place of a conventional FCC was very profitable. The incremental IRR for DCC Type I was 31.1% and 55.6% for DCC Type II. The payout was 2.2 years after tax for DCC Type II and 3.6 years for DCC Type II.



PROPYLENE SENSITIVITY

The price of propylene was varied from +/- 30% of the base price and its impact on the IRR is shown in Figure 1. Even at a propylene price 30% lower than the base value the IRR for DCC Type II is still attractive. The sensitivity to the propylene value is more pronounced for DCC Type I. Although it still appears favorable at propylene values up to 10 % less than the base value.

Figure 1



REVAMP ECONOMICS

Work recently completed in Stone & Websters' Milton Keynes office indicates that a revamp of an existing FCC to an equivalent DCC type I operation (most extreme revamp) can be quite attractive. The majority of the revamp costs were found to be in the regenerator and flue gas system to handle the

additional coke burning capacity. Polymer grade propylene was produced for petrochemical sales. A very attractive pretax payback of 1.5 years was found

CONCLUSION

As the price of propylene remains high there will be continued interest in refinery sourced propylene for petrochemical sales. Based on average prices during the last two years, a new DCC plant for production of propylene provides an attractive return on investment. The sensitivity of the project economics to fluctuations in propylene prices is relatively low.

The integration of DCC technology into a refinery offers an atractive opportunity to produce large quantities of light olefins by the conversion of heavy vacuum gas oils. Thus, providing the refiner with the flexibility to produce either polymer grade propylene or premium gasoline blending components (ie. ethers and alkylate).

Acknowledgement

The author would like to thank Mike Dent and Glenn Johnson for their invaluable assistance in the preparation of this paper.

References

1. 'Deep Catalytic Cracking, Maximize Olefin Production", L.Chapin, W.Letzsch. 1994 NPRA meeting AM-94-43.
2. "A New Propylene Production Process from Heavy Gas Oil", J. Fukang, L. Zaiting, W. Xieqing, M.Enze. 1990 NPRA meeting AM-90-40.
3. 'Propylene from Heavy Gas Oils", J. Bonilla, A. Batachari . Stone & Webster 7th Annual Refining Seminar 1995.
4. 'Propylene in West Europe-An Outlook", Andrew Pettman, CMAI Europe. Dec. 1995.
5. 'Catalytic Cracking to Maximize Light Olefins", D. Hutchinson, R. Hood. Association Francaise Des Techniciens et Professionnels Du Petrole, IFP Dec. 1996.

Table 5
Feedstock and Product Pricing*

Feedstocks	**$/BBL**
Arabian Light	18.47
Isobutane	17.64
Methanol	18.90
MTBE	42.84
Products	
Sulfur (LT)	75.00
Propane	14.35
N-Butane	16.80
Petroleum Coke	25.00
Fuel Gas (FOEB)	9.30
Low Sulfur Diesel	20.89
Kerosine/Jet Fuel	23.12
RFG Gasoline Blend	30.86
Propylene to Sales	45.18

US Gulf Coast Pricing Basis
Sources: The Oil Daily, 28 June 95 & Octane Week, 29 May 95

Table 6
Product Specifications

Propylene	Polymer Grade	
Reformulated Gasoline*	CARB Phase 2 March 1996	Phase 1 Federal Jan 1 1995
• RVP (max)***	7.0	$8.0^{(N)}$ / $7.1^{(s)}$ **
• FON (min)	91.0	91.0
• Olefins (vol%, max)	6.0	9.2
• Aromatics (vol%, max)	25.0	27.0
• Benzene (vol%, max)	1.0	1.0
• Oxygen (wt%, min)	2.0	2.0
• Sulfur (ppm,wt%)	40	339
Diesel		
• Sulfur (wt%, max)	0.05	
• Aromatics (vol%, max)		
• Cetane No. (min)	40.0	
Jet Fuel		
• Sulfur (wt%, max)	0.3	
• Aromatics (vol%, max)	24.0	

* T50 and T90 specs beyond scope of this evaluation
** (N) Northern States, (S) Southern States
*** Summer Season only

CONTROL AND ORIGIN OF NOx IN THE FCCU REGENERATOR
THE PERFORMANCE OF XNOx-2, A COMMERCIAL NOx REDUCTION CATALYST

A. W. Peters, W. Suárez, Manoj Koranne, Carmo Pereira,
G. D. Weatherbee, Xinjin Zhao, S. Davey, and B. Lakhanpal

Grace Davison, Columbia, MD 21044

Keywords: fluid catalytic cracking unit (FCCU) regenerator, carbon monoxide (CO) oxidation, nitrogen oxide (NOx) reduction

Introduction

In this paper we describe the performance of a NOx control additive for the FCCU regenerator. This formulation reduces NOx and at the same time functions as a CO oxidation promoter. The NOx reduction catalyst is added to the total FCC inventory at levels similar to combustion promoter. This promoter has been pilot unit tested in the Davison circulating riser, and the results have been confirmed in commercial testing. Laboratory results suggest that these catalysts decrease NO emissions by chemically reducing the NO with CO in the regenerator to form N_2 and CO_2. While this reaction also occurs to a certain extent in commercial regenerator operation, it is not catalyzed by conventional platinum based CO oxidation promoters.

The Chemistry of NOx in the FCCU Regenerator

The major environmental pollutants from burning coke in the FCCU regenerator include CO (carbon monoxide) and nitrogen and sulfur oxides. Both CO and SOx emissions can be controlled to a low level using relatively small amounts of commercial additives. NO_X emissions are also regulated, but are not so easily controlled. NOx emissions, including NO, NO_2 and N_2O, are typically in the range of 100 ppm to 500 ppm. Since regulations based on regional considerations vary from state to state and even from refinery to refinery, emissions in this range may be outside allowable limits. The NO_2 is formed only after the NO is emitted to the atmosphere, while N_2O is formed in small quantities if at all. Since most of the nitrogen oxides in the regenerator are in the form of NO, the formation and control of NO in the regenerator is the major issue.

The chemistry of NO in the regenerator has recently been described in two independent studies (1,2). Both studies agree in essentials. About half of the nitrogen in the feed appears as coke on the catalyst. The NO in the regenerator derives entirely from burning the nitrogen in the coke during regeneration. At the relatively low temperature in the regenerator, $\leq 800°C$, thermodynamic considerations show that NO is not formed from oxidation of the nitrogen in the air introduced into the regenerator.

The surprise is that only a small percentage of the coke nitrogen is converted to NO during regeneration. Under normal unpromoted regenerator operation most of the nitrogen is converted to N_2. These results were obtained by nitrogen balancing a pilot plant scale FCCU (3) using a relatively high nitrogen feed stock, 0.32% N at relatively high conversions. The catalyst was regenerated using an argon oxygen mixture in place of air, eliminating all sources of molecular nitrogen in the regenerator except from the coke, Table 1.

Table 1. Nitrogen Balance in a pilot plant FCCU. Regeneration with an Ar/O_2 mixture.

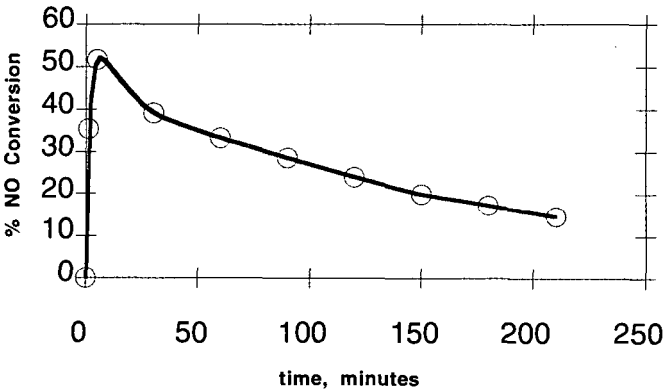
Feedstock:	Moderate Nitrogen	High Nitrogen
N, Wt%	0.13	0.32
Wt. % Conversion	73.9	59.8
Coke, Wt. % of Feed	3.68	4.26
Flue Gas NO,	62 ppm	211 ppm
Flue Gas N_2,	450 ppm	1250 ppm
Recovery of Feed N, %		
in Total liquid product	47.4	50.1
in Coke	35	-
% of Feed N recovered as NO	2.6	2.7
as N_2	38	32.7
Recovery of Regenerator N, %	**5**	**7**
as N_2	**95**	**93**
as NO	**5**	7
Total N Recovery, Wt. %	**88.0**	**85.6**

In this experiment the molecular nitrogen formed in the regenerator was directly measured by gas chromatography. The results show that more than 90% of the nitrogen in the coke forms N_2 rather than NO in an unpromoted regenerator. This means that the nitrogen in the coke is either converted directly to N_2 during regeneration, or is converted to NO and then reduced in the regenerator to N_2. The regenerator contains a variety of reductants including carbon monoxide (CO) and unburned coke on catalyst that has just entered the regenerator as well as residual coke on regenerated or partially regenerated catalyst. CO is present in relatively high concentrations, especially in an unpromoted operation. Although the NO can react with both the coke and the CO, the reaction with the CO to form N_2 and CO_2 is probably the most important. These events explain the observed increase in NO emissions with the addition of CO combustion promoter (less CO in the regenerator), and the decrease in NO_X levels observed with operation in partial burn conditions due to increased amounts of CO as well as coke. A number of NO_X reduction strategies including regenerator design changes based on this chemistry have been described in the patent literature. Some are based on placing more reductant in the regenerator, and in other cases the regenerator flue gas contacts reductant in the form of CO or spent catalyst (4-8).

The Reduction of NO with CO or with Coke on Spent Catalyst.

Previous work has shown that the reaction of NO with coke to form N2 is nearly as rapid as the reaction of oxygen with coke (9). We were able to directly observe the reaction of NO with coke on a spent FCCU catalyst under approximate regenerator conditions, Figure 1.

Figure 1: Reaction Between NO and Coke on Spent Catalyst to form Molecular Nitrogen and CO.



The result of this experiment shows a stiochiometry of approximately 1:1 consistent with the reaction

$$2\,C + 2\,NO = 2\,CO + N_2.$$

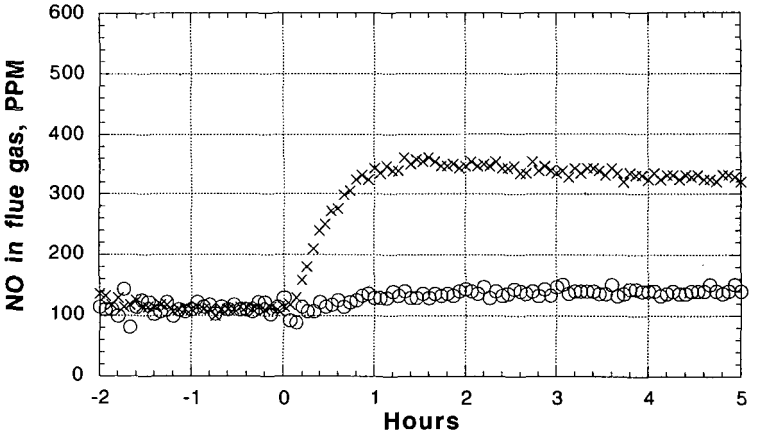
Another possibility is the reduction of NO with CO in the regenerator. Reactor studies show that while NO and CO do not react at regenerator temperatures in an empty reactor or over a low surface area inert, the reaction will occur over equilibrium catalyst, especially with nickel, vanadium and possibly other contaminants. Previous work has shown that high nickel equilibrium catalysts can function as CO oxidation promoters (10). Vanadium on titania is a well known commercial SCR catalyst. This result shows that equilibrium catalysts containing metal can also function as a promoter for the reaction of CO with NO, Table 2.

Table 2. Activity for NO conversion by reduction with CO. Reaction conditions 9,000 GHSV, 1700 ppm NO, CO/NO = 3/1.

Equilibrium Catalyst	A	B
Ni, ppm	378	1598
V, ppm	471	2298
Reactor Temperature, °C	**% Conversion**	
550	0.0	0.0
673	9	24
711	9	45
732	9	56

NO emissions can be reduced by reaction with CO in the regenerator or coke on the catalyst. These reactions form the basis for commercial strategies for NO control such as operation in partial burn, operation with low levels of promotion and higher levels of CO, and a variety of patented processes. However, it is not generally desirable to sacrifice CO conversion or to increase coke on regenerated catalyst for the sake of NOx reduction. Since NOx emissions increase with the addition of CO oxidation promoter, it is important to develop a promoter which catalyzes both the oxidation of CO to CO_2 as well as the reduction of NO to N_2 with CO. The operation of such a promoter, XNOx-2, in a FCC pilot unit is shown in Figure 2. The pilot unit operation is the Davison Circulation Riser (DCR) described elsewhere (11) running a feed stock previously described (1) containing 0.13 wt. % nitrogen.

Figure 2: Comparison of NO emissions in the DCR (Davison Circulating Riser)with a circulating catalyst inventory containing 0.5% of 500 ppm Pt on alumina (x) and 0.5% of XNOx-2 (o).



XNOx-2 and Pt/Alumina Activity for NO Reduction by CO

XNOx-2 works by providing a balanced bifunctional catalytic activity for both the oxidation of CO to CO_2 and for the reaction of CO with NO to produce CO_2 and N_2, controlling both CO and NO emissions. To demonstrate the catalytic basis for this effect we passed CO and NO over XNOx-2 and over a conventional CO combustion promoter containing 500 ppm Pt impregnated on alumina with the results shown in Figures 3 and 4. The activity for CO conversion in the presence of NO over platinum flattens and drops off over 400 °C, while the activity for this reaction over XNOx-2 increases rapidly up to at least 600°C, the highest temperature tested, Figure 3a. The NO conversion plot with temperature shows the same trend, Figure 3b. In this experiment the platinum promoter cannot convert more than 50% of the NO, while the XNOx-2 converts essentially all of the NO. By comparison conversion over Ecat is an order of magnitude or more lower, Table 2.

A plot of CO conversion on one axis and NO conversion on the other axis, Figure 4, is especially interesting. In the case of XNOx-2 we obtain a 45° plot showing one to one conversion. This agrees with the proposed stoichiometry. For every molecule of NO converted, one molecule of CO is converted, the stoichiometry for the desired reaction

$$2CO + 2NO \longrightarrow 2CO_2 + N_2.$$

Over the platinum promoter more NO is converted than CO. This indicates the conversion of NO to nitrogen species other than N_2. The platinum based CO promoters do not promote the reaction between NO and CO very effectively at regenerator temperatures, and the product is not the desired N_2. XNOx-2, on the other hand, is selective for the conversion of NO to N_2 in the presence of CO and at regenerator temperatures.

Figure 3: CO and NO conversion over 500 ppm Pt on gamma alumina (x) and over XNOx-2 (o) at 25,000 GHSV, 1375 ppm NO, and 3000 ppm CO.

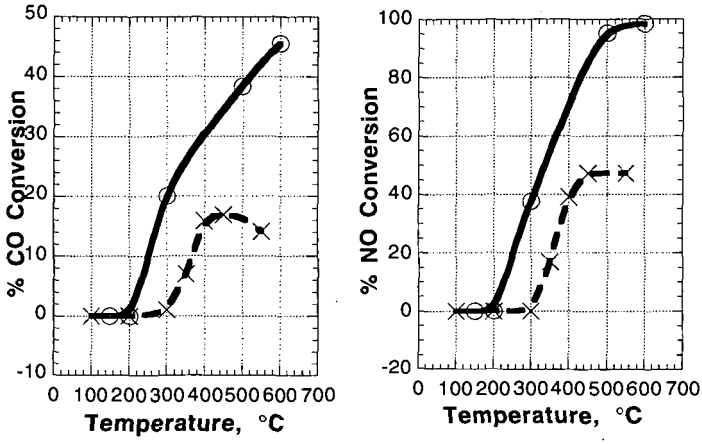
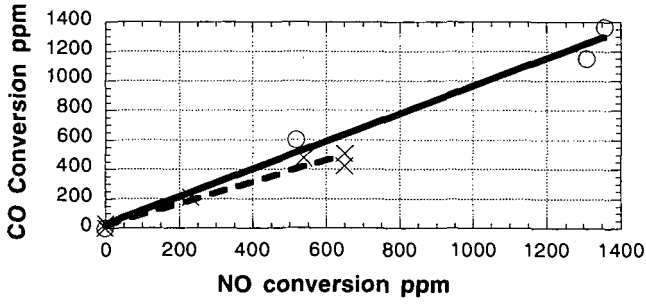


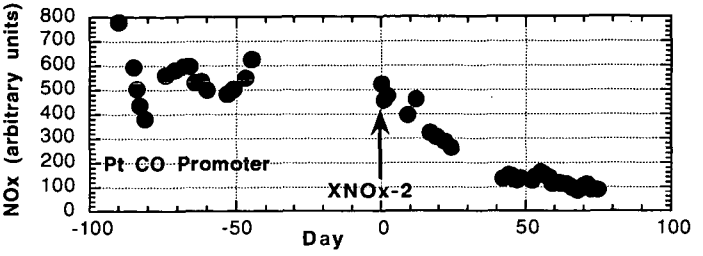
Figure 4: CO and NO stiochiometry for the results in Figure 3.



Commercial Testing

XNOx-2 has been tested in a commercial application currently using a conventional Pt on alumina CO combustion promoter. The conventional combustion promoter was discontinued and XNOx-2 begun at day zero shown in Figure 5. NOx emissions decreased slowly over a period of thirty days from a level of 500 units to a level of about 150 units, a drop of about 70%. During this period of time the afterburn, a measure of CO promotion efficiency, remained within normal limits. The commercial NOx reduction is somewhat greater than observed in DCR testing. The reason for this is probably the poorer mixing and higher localized CO concentrations in the commercial regenerator. In regions of high CO concentration the XNOx-2 will be especially effective.

Figure 5: Commercial test of the combustion promoter XNOx-2 compared to a conventional Pt on alumina promoter.



Acknowledgment

We would like to acknowledge the valuable laboratory work and the useful suggestions of Kevin Kreipl and Cathy Smith in the execution of the work described in this paper.

References

(1) A. W. Peters, G. D. Weatherbee, and Xinjin Zhao, Fuel Reformulation, Volume 5, No. 3, May/June 1995, p.45-50.
(2) S. Tamhankar, R. Menon, T. Chou, R. Ramachandran, R. Hull, and R. Watson, Oil and Gas Journal, March 4, 1996, p. 60-68.
(3) G. W. Young, in Fluid Catalytic Cracking: Science and Technology, Studies in Surface Science and Technology, J. S. Magee and M. M. Mitchell, Jr., eds., Elsevier, 1993, p.257.
(4) An example is a counter-current regenerator design by Kellogg claimed to reduce NOx by 50% or more. Spent catalyst is distributed over the top of the regenerator bed. NO reacts with the coke on the spent catalyst.
(5) A. R. Hansen, M. N. Harandi, D. L. Johnson, P. H. Schipper, S. A. Stevenson, Conversion of NOx in FCC Bubbling Bed Regenerator, US 5382352, 1995.
(6) J. S. Buchanan and D. L. Johnson, FCC Regeneration Process with Low NOx CO Boiler, US 5372706 (1994).
(7) P. H. Terry, Fluid Catalytic Cracking System, US 5360598, (1994).
(8) H. Owen and P. H. Schipper, Regeneration with Partial CO Combustion, US 5077252.
(9) Xi Chu and L. D. Schmidt, Ind. Eng. Chem. Res., 1993, **32**, 1359-1366.
(10) P. K. Doolin, J. F. Hoffman, and M. M. Mitchell Jr., Appl. Catal., 71 (1991) 233.

FCCU Regenerator Lab-Scale Simulator for Testing New Catalytic Additives for Reduction of Emissions from the FCC Regenerator

George Yaluris, Xinjin Zhao, Alan W. Peters
W. R. Grace & Co.-Conn.
Washington Research Center
7500 Grace Dr., Columbia, MD 21044

Keywords: Fluid catalytic cracking unit (FCCU) regenerator lab-scale simulator, combustion promoter, NO_x reduction

Introduction

Catalyst additives are commonly used in the FCC regenerator to control CO, SO_x and NO_x emissions (1). For example, Pt based combustion promoters are typically used to reduce CO emissions. The development of DESOX® technology has provided refiners with catalyst additives that can reduce the SO_x emissions (2-4). Recent environmental regulations have increased the importance of such catalyst additives in the FCC process and the need to develop new FCCU regenerator additives (5). Due to the lack of a realistic lab-scale simulator of the FCCU regenerator, most of the work in developing catalyst additives for the regenerator has been conducted using either refinery FCC units or pilot plants (e.g., Davison Circulating Riser (DCR), an adiabatic riser with continuous catalyst regeneration) (6,7). The efforts to develop new catalyst additives can be facilitated by the development of a lab-scale unit that simulates the FCCU regenerator. This simulator would allow us to examine the regenerator chemistry and the mechanisms through which additives affect gas emissions, as well as routinely test new additives. In this paper we present the development of such a lab-scale simulator of the FCCU regenerator and its use in testing combustion promoter additives.

Lab-Scale Simulator Unit of FCCU Regenerator

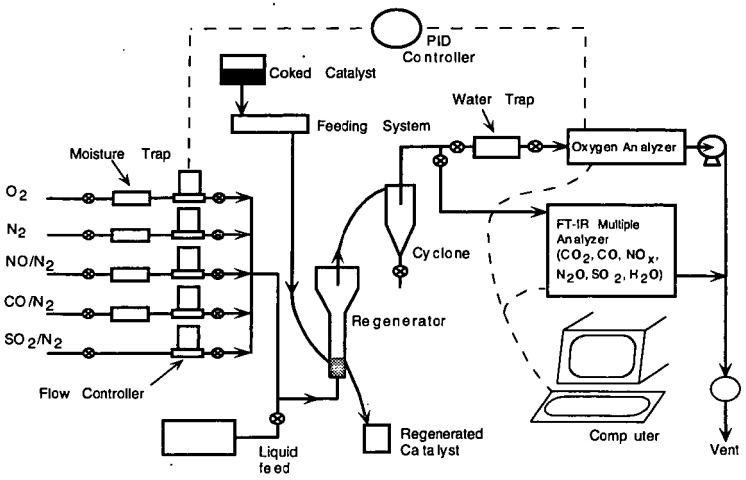
Attempting to simulate all of the operational characteristics of refinery-scale regenerators, which vary significantly in design, in a small lab-scale unit is not practical. For example, it is difficult to simulate the catalyst and gas flow patterns of a large regenerator in an idealized lab-scale reactor, and to simulate the true condition of the catalyst and additives entering the regenerator from the stripper. Thus, we have designed a one-pass system that utilizes pre-coked catalyst, operates as close as possible to the operation conditions of refinery regenerators, captures the chemical phenomena occurring in a true regenerator, and predicts the performance of catalyst additives.

The main characteristics of the lab-scale simulator unit of the FCCU regenerator (FCCU-RSU) are:

1. Fluidization of the FCC catalyst and additives
2. Continuous coked catalyst flow through the reactor and ability to control the catalyst residence time in the reactor
3. Control of the excess oxygen in the reactor effluent
4. Control of the temperature of the exothermic coke burning reaction
5. Ability to conduct mechanistic and kinetic experiments to probe the regenerator chemistry (formation of CO, SO_x and NO_x) and the mechanism through which catalyst additives work

In Figure 1 we show a schematic diagram of the FCCU-RSU we have built. The system consists of a quartz glass tube reactor (2.54 cm diameter) with a gas-catalyst particles disengagement section at the top. Further, separation of catalyst fines is achieved in the cyclone that follows the reactor. A custom designed oven allows control of the reactor temperature during the fast exothermic coke burning reaction. Air, oxygen, nitrogen, CO, NO, SO_2, and evaporated liquid feed can be fed in the reactor. Typically, nitrogen is used to fluidize the catalyst bed. Emission gases, like CO, NO and SO_2, are used in kinetic and mechanistic experiments to study the interactions between these gases, the catalyst, and the additives. A

Figure 1: Schematic diagram of FCCU regenerator lab-scale simulation.



portion of the reactor effluent is sent to a Horiba oxygen analyzer (MPA-510), and through a feedback loop a PID controller controls the amount of air or oxygen needed to maintain the desired excess oxygen in the effluent. All other reactor gas products are analyzed by an On-Line Technologies 2002 FTIR Multigas analyzer which can measure CO_2, CO, NO, N_2O, NO_2, SO_2, H_2O and other FTIR-active gases. The catalyst flows continuously through the reactor using a custom-designed catalyst flow system purged with nitrogen to avoid contamination of reaction products with atmospheric gases. The catalyst residence time in the reactor depends on the catalyst flow rate, and can be controlled from about 5 min to more than 2 h. Detailed mixing experiments showed that mixing in the reactor is close to that of a CSTR.

Experimental

Using the FCCU-RSU we studied the performance of conventional Pt-based CO combustion promoters as well as that of new non-conventional additives that combine the CO combustion promotion functionality with reduction of NO_x from the regenerator (XNOx™ additives). The additives were used in our studies as synthesized both after calcination in air at 773 K and after reduction at 773 K in flowing 4% H_2 in N_2. Commercial FCC catalysts were coked in our pilot plant (DCR) using a resid FCC feed (API @ 60 °F: 20.6) that contains 0.41% sulfur, 0.18% total nitrogen, 0.06% basic nitrogen, and 5.1% Conradson carbon. The coked catalysts contained *ca.* 0.9 - 2.5% coke. The additives were added to the catalyst at the level of 0.5 wt%. Before charging the catalyst to the catalyst feed system, the catalyst was dried overnight at 373 K.

Typically the catalyst residence time in the reactor was about 16 min, and the excess oxygen was controlled at 1.1%. Unless otherwise noted, the reaction temperature was varied from 973 K to 1003 K. Data was collected for 30 - 60 min after steady state had been achieved.

Results

The results of coked catalyst regeneration in the FCCU-RSU show that the unit simulates well the catalyst regeneration process in the refinery regenerator. The CO/CO_2 ratio is a strong function of temperature and excess oxygen and decreases with increasing temperature and increasing excess oxygen. In Figure 2 we show that the amounts of CO detected in the flue gas follow inversely the amount of excess oxygen. At 1043 K, CO_2 increases from 1.6% to 3.0% to 4.4% as the catalyst flow increases from 0.47 to 1.07 to 1.67 g/min. Figure 2 shows that as the catalyst flow increases (catalyst residence time decreases) the amount of SO_2 increases roughly proportional to the increase in catalyst flow. These results are an

Figure 2: Composition of reactor effluent gas during regeneration of an FCC catalyst containing about 2.5% coke. CO, NO, SO_2 in ppm. Excess O_2 in %. Reactor temperature 1043 K.

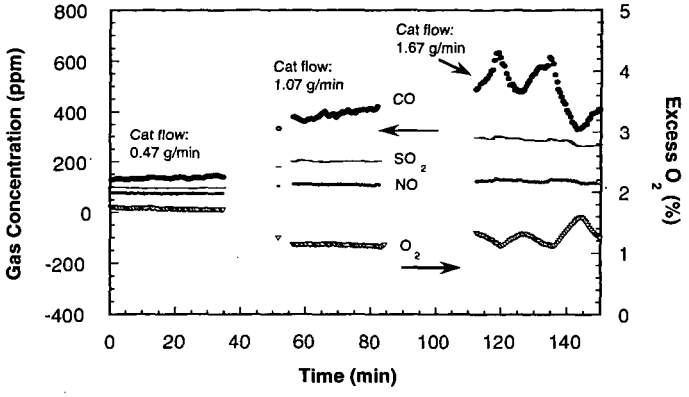
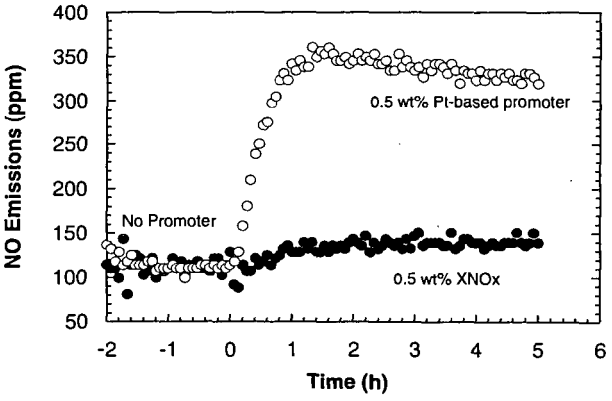


Figure 3: NO emissions from the pilot plant (DCR) regenerator when Pt-based and XNOx™-based combustion promoters are added in the catalyst (at 0 h)at 0.5 wt% additive level. Typical DCR regenerator temperature is 977 K.



indication that at the temperature of this experiment most combustion of coke occurs during the first few minutes of the catalyst residence time in the regenerator. CO also increases with decreasing catalyst residence time, but its concentration in the flue gas depends on oxygen flow as well. NO increases as more coked catalyst is fed to the reactor. However, because of its reaction with CO, it does not increase in proportion to the catalyst flow increase.

According to refinery as well as our pilot plant experience (8), when Pt-based combustion promoters are added in the regenerator to reduce CO emissions, NO_x emissions increase. In DCR testing (Figure 3), the addition of Pt-based promoter in the regenerator increased NO formation during the cracking of a light paraffinic feed by about 3 times. In agreement with these results, the FCCU-RSU also shows a dramatic increase of NO_x in the reactor effluent when a Pt-based combustion promoter is added to the coked catalyst at the level of 0.5 wt%. The magnitude of the increase in the amount of nitrogen oxides produced depends on the reactor temperature and can be as high as five fold (Table 1)

Recently we developed new combustion promoter technology (8) that can achieve similar reduction of CO emissions from the FCCU regenerator as can be

Table 1: Average amounts of gas formation during FCC coked catalyst regeneration (1.2 wt% coke) with or without combustion promoter additives. Values shown are in cc/g catalyst passed through the reactor, averaged over 30 - 60 min after the unit has achieved steady state.

Promoter	Nominal Bed Temp (K)	CO_2	CO	N_2O	NO	SO_2	Nitrogen Oxides (%) Change	Effect on CO (%) Change
None	973	11.7	9.74	0.008	0.039	0.080	0	0
Pt-based oxid.	973	18.9	1.59	0.003	0.251	0.061	435	84
Pt-based red.	973	18.0	1.36	0.002	0.245	0.056	420	86
XNOx™ oxid.	973	17.2	2.45	0.004	0.169	0.021	264	75
XNOx™ red.	973	18.0	2.52	0.003	0.173	0.020	270	74
None	988	18.2	3.75	0.031	0.065	0.086	0	0
Pt-based oxid.	988	19.7	1.51	0.005	0.255	0.066	171	60
Pt-based red.	988	20.7	1.41	0	0.260	0.067	172	62
XNOx™ oxid.	988	19.5	1.83	0.008	0.188	0.027	105	51
XNOx™ red.	988	19.9	1.95	0.008	0.186	0.025	103	48

achieved with Pt-based promoters, while it produces a significantly smaller increase in NO_x emissions. We tested in the DCR a non-conventional combustion promoter based on XNOx™ technology (Figure 3). With the new combustion promoter in the DCR regenerator, NO emissions increased only 20%. The lab-scale simulator of the FCC regenerator qualitatively gives the same performance results. When XNOx™ is added to the coked catalyst at 0.5 wt%, nitrogen oxides in the flue gas increase about 40% less than the increase measured for the Pt-based additive (Table 1).

The observed reduction in nitrogen oxide emissions is achieved at only a slight cost in CO combustion promotion (Table 1). When the formulation of the XNOx™ combustion promoter is adjusted to achieve the same combustion promotion as the Pt-based additive, the FCCU-RSU still shows that, compared to the Pt-based additive, the XNOx™ additive achieves similar decreases in the concentration of nitrogen oxides in the reactor effluent to those shown in Table 1. Thus, the reduced NO_x achieved with the use of XNOx™ combustion promoters is a result of the additive's unique chemistry and not due to an increase of the CO reaction with NO that may result from the small increase of CO in the reactor. It is worth noting that according to the data in Table 1, significant amounts of N_2O are formed only in the absence of combustion promoters. Apparently, when these additives are present in the reactor, N_2O is rapidly oxidized to NO.

In an FCCU, the combustion promoters enter the regenerator after being reduced in the riser. To determine if the oxidation state of the additive affect its performance, we tested both oxidized and reduced additives. Our results (Table 1), indicate that, at least in the FCCU-RSU, the oxidation state of the additive does not have a significant impact on either the CO combustion promotion or the observed increase in NO_x. This result does not imply that the redox properties of the additive do not impact the flue gas composition. We speculate that upon entering the reactor, at the conditions of these experiments (>973 K, >1% O_2, and CO present), the additive rapidly reaches its equilibrium oxidation state. The presence of redox catalytic cycles involving surface sites and O_2, CO, NO and other nitrogen species may then play a role in determining the amount of nitrogen oxides produced during catalyst regeneration.

Conclusions

We have developed a lab-scale simulator of the FCCU regenerator that can be used to study the performance of FCC regenerator catalyst additives, and investigate the mechanism (e.g., role of additive's oxidation state) and kinetics through which these additives affect the formation of carbon, nitrogen and sulfur oxides. The lab-scale system includes a custom-designed fluidized bed reactor and catalyst flow system, and allows control of the important operation parameters (catalyst residence time, excess oxygen, reactor temperature). Coked catalyst

regeneration experiments and performance tests of conventional and non-conventional combustion promoters show that the FCCU-RSU can simulate the operation and capture the chemistry of the FCCU regenerator.

References:

1. Bhattacharyya, A.A., and Yoo, J.S. *in* "Fluid Catalytic Cracking: Science and Technology" (Magee, J.S. and Mitchell, M.M., Jr. Eds.), *Stud. Surf. Sci. Catal.* Vol. 76, p. 531 . Elsevier Science Publishers B. V., Amsterdam, 1993.
2. Lane, P.A., and Latimer, J.A. *in* "Advanced Fluid Catalytic Cracking Technology" (Chuang, K.C., Young, G.W. and Benslay, R.M. Eds.), *AIChE Symp. Ser., No. 291* Vol. 88, p. 76. American Institute of Chemical Engineers, New York, 1992.
3. Yoo, J.S.,Karch, J.A.,Radlowski, C.A., and Bhattacharyya, A.A. *in* "Catal. Sci. Technol., Proc.," Tokyo, 1990, (Yoshida, S., Takezawa, N. and Ono, T. Eds.), , p. 183. Kodansha , Tokyo, 1991.
4. Yoo, J.S.,Bhattacharyya, A.A.,Radlowski, C.A., and Karch, J.A., *Appl. Catal., B* **1(3),** 169 (1992).
5. Evans, R.E., and Quinn, G.P. *in* "Fluid Catalytic Cracking: Science and Technology" (Magee, J.S. and Mitchell, M.M., Jr. Eds.), *Stud. Surf. Sci. Catal.* Vol. 76, p. 563. Elsevier Science Publishers B. V., Amsterdam, 1993.
6. Peters, A.W.,Weatherbee, G.D., and Zhao, X., *Fuel Reformulation* **5(3),** 45 (1995).
7. Young, G.W. *in* "Fluid Catalytic Cracking: Science and Technology" (Magee, J.S. and Mitchell, M.M., Jr. Eds.), *Stud. Surf. Sci. Catal.* Vol. 76, p. 257 . Elsevier Science Publishers B. V., Amsterdam, 1993.
8. Davey, S.W., and Haley, J.T. *in* "Oil & Gas Journal International Catalyst Conference and Exhibition," Houston, Texas, February 1-2, 1996.

Mesoporous Zeolite-Supported Noble Metal Catalysts for Low-Temperature Hydrogenation of Aromatics in Distillate Fuels

Kondam Madhusudan REDDY and Chunshan SONG*

Fuel Science Program, Department of Materials Science and Engineering
209 Academic Projects Building, The Pennsylvania State University
University Park, PA 16802, USA

Keywords: Mesoporous zeolite, Catalyst, Noble Metals, Hydrogenation, Fuels

Introduction

The present work is concerned with deep hydrogenation of aromatics in distillate fuels at low temperatures using mesoporous zeolite-supported noble metal catalysts. This work is a part of our on-going effort to develop advanced thermally stable jet fuels from coal-derived liquids and petroleum. Saturation of naphthalene and its derivatives not only reduces aromatics contents of jet fuels, but also generates decalins which show much higher thermal stability than long-chain alkanes in jet fuels at high temperature (Song et al., 1994). This work also has a bearing on developing new catalytic processes for low-temperature hydrogenation of distillate fuels.

The Clean Air Act Amendments of 1990 and new regulations call for the production and use of more environmentally friendly transportation fuels with lower contents of sulfur and aromatics (Lee et al., 1993; Unzelman, 1993). High aromatic content in distillate fuels lowers the fuel quality and contributes significantly to the formation of environmentally harmful emissions (Stanislaus and Cooper, 1994). California Air Resources Board (CARB) has passed legislative measures to limit the sulfur and aromatic contents of diesel fuel to 0.05 wt% and 10 vol%, respectively, effective October 1993 (Lee et al., 1993). Currently, conventional hydrotreating technology is adapted for aromatics saturation. Some studies have shown that complete hydrogenation of aromatics is not possible owing to equilibrium limitations under typical hydrotreating conditions, and existing middle distillate hydrotreaters designed to reduce sulfur and nitrogen levels would lower the diesel aromatics only marginally (Stanislaus and Cooper, 1994).

Deep hydrogenation may become necessary in the near future for reducing aromatic contents of distillate fuels to meet increasingly more stringent regulations. One of the significant findings by The US Auto/Oil Air Quality Improvement Research Program (which involved Ford, General Motors, Chrysler, and 14 largest US petroleum companies) is that lowering aromatic content lowers toxic emissions (Kreucher, 1995; Unzelman, 1993). The significant findings of the European Program on Emissions, Fuels, and Engine Technologies (EPEFE) also include the following related to aromatics: 1) decreasing aromatics reduces catalytic converter light-off time, improves the converter efficiency and decreases exhaust hydrocarbons; and 2) decreasing fuel polyaromatics reduces light-duty diesel exhaust nitrogen oxides and particulate material and heavy-duty exhaust hydrocarbons, nitrogen oxides, and particulate material (Kreucher, 1995).

Typical conventional catalysts for fuel hydroprocessing are sulfided Co-Mo and Ni-Mo supported on alumina. However, such catalysts are active only at relatively high temperatures (e.g., >300°C). Because hydrogenation is exothermic, deep hydrogenation is favored at lower temperature. It is therefore natural to consider deep hydrogenation at low temperatures (e.g., ≤300°C), and the potential candidate catalysts for low-temperature hydrotreating include noble metals. Since it is known that noble metal catalysts are easily deactivated by sulfur compounds, a two-stage processing strategy may be adopted. The first stage would involve deep desulfurization of the fuels using metal sulfide catalysts, and the second stage deals with deep hydrogenation over noble metal catalysts. Such a two-stage processing scheme may become practically applicable, since deep desulfurization is likely to be required by regulations to further reduce sulfur contents of transportation fuels in the near future.

The objective of this work is to explore the potential of mesoporous zeolite as support of noble metal catalysts for deep hydrogenation of aromatics in jet fuel and diesel fuel. Recently, Mobil researchers have invented MCM-41 type mesoporous molecular sieves possessing a hexagonal array of uniform mesopores (Beck et al., 1992; Kresge et al., 1993). We have synthesized mesoporous zeolites with MCM-41 type structure using three different aluminum sources (Reddy and Song, 1996a, 1996b). We are currently exploring their applications for catalytic fuel processing (Reddy and Song, 1996b; Song and Reddy, 1996). In our preliminary work, Pt/MCM-41 catalysts containing 3 wt% Pt were prepared with the mesoporous zeolites synthesized using pseudo boehmite, Al isopropoxide, and Al sulfate, and applied for hydrogenation of naphthalene at 200°C and that of phenanthrene at 300°C. The results showed that the sample made by using Al isopropoxide gives the best catalyst (Reddy and Song, 1996b). In the present work, supported catalysts containing 2 wt% Pt or 2 wt% Pd were prepared using proton-form MCM-41

* Corresponding author. E-mail: csong@psu.edu; Tel: 814-863-4466; Fax: 814-865-3075

(synthesized using Al isopropoxide) as well as Al_2O_3 and TiO_2 as the support materials. This paper reports on their performance for hydrogenation of naphthalene in n-tridecane at 200°C.

Experimental

Catalyst Preparation

The mesoporous zeolite with MCM-41 type structure was synthesized using aluminum isopropoxide as the Al source according to the procedure described elsewhere (Reddy and Song, 1996). Supported catalysts containing 2 wt% Pt or 2 wt% Pd were prepared using proton-form mesoporous MCM-41 zeolite as well as Al_2O_3 and TiO_2 as the support materials. Table 1 gives their properties. The Pt catalysts were prepared by impregnation from aqueous solution of hydrogen hexacholoro platinate (IV) hydrate, $H_2PtCl_6xH_2O$ (Aldrich, 99.995% Pt, metal basis). The Pd catalysts were prepared by impregnation of $PdCl_2$ (Aldrich, 99.999% Pd, metal basis) dissolved in dilute hydrochloric acid (sufficient to form soluble $PdCl_4^{2-}$). In both cases, water was removed by rotary evaporation at about 60°C. The catalyst precursors were dried in an oven at 60°C over night, and then calcined in an electric furnace at 450°C for 4 h. The nominal metal concentration was kept at 2 wt% for both Pt and Pd catalysts. Metal reduction was done in situ during naphthalene hydrogenation tests.

Catalyst Evaluation

All the catalysts were tested at 200 °C for a given residence time in 25-mL stainless-steel microautoclaves. The total volume of the system including the connecting tube between reactor and pressure gauge is about 30 mL. Typically, the reactor was charged with 1.0 g naphthalene (Aldrich, 99%), 4.0 g n-tridecane solvent, and 0.1 g catalyst. The charged reactor was flushed with H_2, then pressurized to 1000 psig (cold) to start the test. The reactor was mounted on a holder, immersed in a fluidized sand bath preheated to 200°C, and shaken vertically at 240 cycles/min with a 1 cm stroke.

At the end of the test, the reactor was taken out of the sandbath, quenched in cold water, and then allowed to cool down in air to room temperature. The gaseous products were collected for analysis and then the reactor was opened. The contents of the reactor were washed with acetone onto a filter. Solution products were analyzed by GC-MS and GC-FID. The capillary columns were 30mx0.25mm DB-5 (J&W Scientific) for GC-MS and 30mx0.25mm DB-5 (Hewlett-Packard), for GC-FID and the oven temperature program for both GC instruments was 60-280 °C at 10 °C/min. GC and GC-MS indicate that cracking or isomerization of n-tridecane, if any, were negligible. The yields of products were determined by quantitative GC analysis using *n*-nonane as internal standard, and the conversion was determined by the amount of naphthalene recovered after the reaction.

Selected tests were conducted to examine the effect of pre-reduction. Pre-reduction was carried out at 200°C for 1 h under reaction conditions except that naphthalene was not present during the reduction stage. After the reduction, the reactor was cooled down to ambient temperature, vented and opened. The reactor was re-sealed after the addition of 1 g naphthalene, and re-pressurized to 1000 psig H_2 at room temperature. Hydrogenation over the pre-reduced catalysts was also conducted at 200°C for 0.5 h.

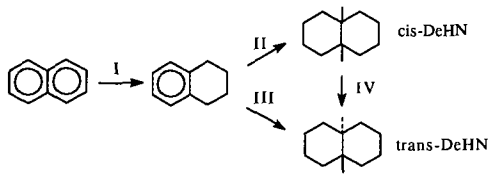
Table 1. Properties of the Mesoporous MCM-41 Zeolite, Titania and Alumina Supports

Support ID	Material Type	Surface Area, m^2/g	Pore Vol cc/g	SiO_2/Al_2O_3 mol ratio	Source
MCM-41	Mesoporous zeolite	1206	1.77	40.7	PSU Fuel Science, Synthesized with Al
TiO_2	Titania	53	---	---	Degussa, Titania P25
Al_2O_3	γ-Alumina	113	---	<0.001	Degussa, Aluminum Oxide C

Results and Discussion

Table 2 shows the distribution of products from naphthalene hydrogenation over Pd and Pt catalysts at 200°C for 60 min. The main products from naphthalene hydrogenation were tetrahydronaphthalene (tetralin or THN), and cis- and trans-decahydronaphthalene (decalin or DeHN). Δ9,10-octalin was also detected as a minor product in many tests, which is an intermediate from tetralin to decalin. The selectivity to tetralin+decalin+octalin approaches to unity in all the runs, indicating that there were essentially no side reactions such as ring-opening cracking

and ring-contraction isomerization under the conditions. Based on the present and previous results (Lai and Song, 1996; Schmitz et al., 1996), the reaction pathways can be represented by Scheme I.



Scheme I

Effect of Supports

For Pt catalysts on different supports, the yield of tetralin decreased in the order of alumina > titania > MCM-41, whereas the yields of trans- and cis-decalins increased in the order of alumina < titania < MCM-41. In the case of Pt/MCM-41, the intermediate product tetralin was almost completely hydrogenated, whereas tetralin still remains as a major product with Pt/Al_2O_3 and Pt/TiO_2.

Table 2 Hydrogenation of Naphthalene at 200°C for 60 min over Pt and Pd Catalysts

Expt ID	79	115	81	82	83	84
Catalyst	Pt/Al_2O_3	Pt/TiO_2	Pt/MCM-41	Pd/Al_2O_3	Pd/TiO_2	Pd/MCM-41
Conversion (%)	98.3	99.9	100.0	99.9	99.9	100.0
Selectivity (wt%)						
Tetralin	57.0	35.8	0.0	42.5	30.5	0.0
9,10-Octalin	0.8	1.0	0.0	0.7	0.3	0.0
trans-Decalin	10.6	14.9	50.2	34.6	43.9	64.4
cis-Decalin	31.1	47.9	49.4	22.0	25.1	35.4
Others	0.5	0.4	0.4	0.2	0.2	0.2
trans-/cis-DeHN	0.3	0.3	1.0	1.6	1.7	1.8
DeHN+Tetralin	98.7	98.6	99.6	99.1	99.5	99.8
DeHN/Tetralin	0.7	1.7	2444.3	1.3	2.3	1235.3

For Pd catalysts, we observed essentially the same trends in terms of catalytic activity reflected by the increasing yields of decalins or decreasing yields of tetralin. Moreover, both Pd/MCM-41 and Pt/MCM-41 catalysts promoted the hydrogenation to completion such that the dominant products are trans- and cis-decalin, whereas tetralin is still one of the major products with both Al_2O_3- and TiO_2-supported Pd and Pt catalysts. These results indicate MCM-41 supported Pt and Pd catalysts are more active than titania and alumina supported catalysts.

The higher activity of the mesoporous zeolite-supported Pt and Pd may be due to better dispersion of the noble metals on MCM-41, since it has much larger surface than that of Al_2O_3 and TiO_2 supports (Table 1). According to a recent report (Koussathana et al., 1991), hydrogenation of naphthalene and benzene is insensitive to the geometric structure of the Pt species. The mild acidity of MCM-41 may also be a contributing factor, since it contributes to the electron deficiency of the metal on zeolite surface. It is known that noble metals on Y-zeolite and mordenite are often better dispersed and electron deficient as compared to those on alumina (Stanislaus and Cooper, 1994). The zeolitic protons can act as chemical anchors for reduced noble metal particles (Satchler and Zhang, 1993).

The selectivity to decalin isomers depends on the support and metal type. Compared to Pd/Al_2O_3 and Pd/TiO_2 catalysts, Pd/MCM-41 catalyst afforded higher trans/cis ratio, indicating a higher selectivity to trans-decalin. There appears to be one major difference between Pt and Pd catalysts in selectivity: Pd shows higher selectivity to trans-decalin. Therefore, among the three supports, MCM-41 corresponds to higher trans/cis ratios. Among the two metals, Pd catalysts always afford higher trans/cis ratios. Overall, MCM-41 supported Pd catalyst display highest selectivity to trans-decalin.

Effect of Reaction Time

Since complete naphthalene conversion was reached in 1 h, we reduced the residence time and conducted 30 min runs at 200°C. Table 3 shows the results. Although unreduced catalysts were used, nearly complete naphthalene conversion was achieved in all the runs within 30 min. However, the product distribution changed with residence time. Yields of tetralin increased and decalin yields decreased with decreasing residence time. It is also clear that the absolute yields of tetralin and decalins strongly depended on the type of support and metal.

Even with reduced residence time, the MCM-41 supported Pt and Pd catalysts are substantially more active than the corresponding catalysts supported on alumina and titania (Table 3). In general, the activity of both Pt and Pd catalysts for complete hydrogenation of naphthalene to decalin decreased in the following order with respect to the support type: MCM-41 > TiO_2 > Al_2O_3.

Table 3 Hydrogenation of Naphthalene at 200°C for 30 min over Pt and Pd Catalysts

Expt ID	109r	110	92	93	94	111r
Catalyst	Pt/Al_2O_3	Pt/TiO_2	Pt/MCM-41	Pd/Al_2O_3	Pd/TiO_2	Pd/MCM-41
Conversion (%)	97.2	99.9	100.0	99.9	100.0	99.9
Selectivity (wt%)						
Tetralin	68.9	51.9	0.1	81.3	62.6	17.1
9,10-Octalin	1.1	0.2	0.00	0.9	1.0	0.3
trans-Decalin	6.5	8.2	45.2	10.3	21.1	52.8
cis-Decalin	23.3	39.0	54.3	7.4	15.1	29.7
Others	0.2	0.7	0.6	0.1	0.2	0.1
trans-/cis-DeHN	0.3	0.2	0.8	1.4	1.4	1.8
DeHN+Tetralin	98.7	99.1	99.4	99.0	98.8	99.6
DeHN/Tetralin	0.4	0.9	2160.2	0.2	0.6	4.8

When compared to the 60 min-runs, the yields of tetralin were generally higher and decalin yields lower in 30 min-runs, particularly when Pt or Pd was supported on alumina or titania. The trans/cis ratios of the decalin isomers are lower in the 30 min runs than in 60 min runs, even in the case of Pt/MCM-41 where tetralin was completely converted to decalin within 30 min. These results are consistent with Scheme I and indicate that cis-decalin isomerizes into trans-decalin during the hydrogenation reaction over MCM-41 supported catalysts, being consistent with the previous results from this laboratory (Lai and Song, 1996; Schmitz et al., 1996). TPD of n-butylamine indicates that hydrogen MCM-41 is acidic, but its acidity is lower than that of hydrogen Y zeolite. It appears from comparative examination that the presence of Pd metal and acid sites facilitates both tetralin hydrogenation and cis-decalin isomerization into trans-decalin.

Effect of Pre-Reduction

The above results clearly indicate that both Pd and Pt catalysts supported on the mesoporous MCM-41 are superior over those supported on Al_2O_3 and TiO_2. It should be noted that there may be two contributing factors, since the calcined catalysts were applied without reduction pretreatment. First, the in situ generation of active metal particles by H_2 reduction may be slower in Al_2O_3- and TiO_2-supported Pt and Pd than in MCM-41 supported metals. Second, the reduced metal species on MCM-41 are more active than those on Al_2O_3 and TiO_2. To see if this is the case, we examined the effect of pre-reduction under reaction conditions (hydrogenation over the pre-reduced catalysts at 200°C for 0.5 h).

The results showed that even after pre-reduction, the MCM-41 supported Pt and Pd catalysts are considerably more active than the corresponding Al_2O_3- and TiO_2-supported Pt and Pd catalysts. The differences between the MCM-41 supported catalysts are that pre-reduced Pd/MCM-41 displayed higher activity for tetralin hydrogenation than pre-reduced Pt/MCM-41, whereas the in-situ reduced Pd/MCM-41 was less active than the in-situ reduced Pt/MCM-41. Our previous results of XRD suggested that the zeolite-supported Pt and Pd catalysts were completely reduced after 60 min or 30 min under comparable conditions (Reddy and Song, 1996; Schmitz et al., 1996). Therefore, it is considered that essentially all the noble metal species would have been reduced to metallic particles by a pre-reduction treatment at 200°C for 60 min under an initial H_2 pressure of 1000 psig using n-tridecane solvent. Another puzzling observation was that the pre-reduced catalysts are not always as active as the in-situ reduced catalysts under the reaction conditions employed in this work. Further study is in progress.

Conclusions

Mesoporous MCM-41 zeolite that was synthesized by a proper method may be used as a very effective support for noble metal catalysts. For hydrogenation of naphthalene in n-tridecane at 200°C, both the Pt and Pd catalysts supported on MCM-41 zeolite are substantially more active than the corresponding catalysts supported on Al_2O_3 and TiO_2. In general, the activity of both Pt and Pd catalysts for complete hydrogenation of naphthalene to decalin decreased in the following order with respect to the support type: MCM-41 > TiO_2 > Al_2O_3.

Both Pd/MCM-41 and Pt/MCM-41 catalysts promoted the hydrogenation to completion such that the dominant products are trans- and cis-decalin, whereas tetralin is still one of the major products with both Al_2O_3- and TiO_2-supported Pd and Pt catalysts. In general, Pd catalysts showed higher selectivity to trans-DeHN, whereas higher selectivity to cis-DeHN was displayed by Pt catalysts.

The selectivity to decalin isomers also depends on the support and metal type. Among the three supports, MCM-41 gives higher trans/cis ratio. Among the two metals, Pd affords higher trans/cis ratio. In other words, Pd catalysts showed higher selectivity to trans-decalin, whereas higher selectivity to cis-decalin was displayed by Pt catalysts.

Acknowledgments

We are very grateful to Prof. H. H. Schobert for his encouragement and support. Financial support was provided by US Department of Energy, Pittsburgh Energy Technology Center, and US Air Force, Wright Laboratories. We wish to thank Mr. W. E. Harrison III of USAF and Dr. S. Rogers of DOE for their support, Drs. W.-C. Lai, A. Schmitz and S.-D. Lin for helpful discussions, and Degussa Corporation for providing alumina and titania supports.

References

Beck, J. S., J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, and J. C. Schlenker. J. Am. Chem. Soc., 1992, 114, 10834.

Koussathana, M., D. Vamvouka, H. Economou and X. Verykios. Appl. Catal., 1991, 77, 283.

Kresge, C. T., M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, Nature, 1992, 359, 710-712.

Kreucher, W. M. Chem. Ind., 1995, Aug 7, 601.

Lai, W.-C. and Song, C. Catalysis Today, 1996, in press.

Lee, S. L., Wind, M. De, Desai, P. H., Johnson, C. C., and Mehmet, Y. Asim. Fuel Reformulation, 1993, May/June, 26.

Lin, S.D., and Song, C. Catalysis Today, 1996, in press.

Reddy, K. M. and Song, C. Catalysis Letters, 1996a, 36, 103.

Reddy, K. M. and Song, C. Catalysis Today, 1996b, in press.

Satchtler, W. M. H. and Z. Zhang, Adv. Catal., 1993, 39, 129.

Schmitz, A., Bowers, G. and Song, C. Catalysis Today, 1996, in press.

Song, C., Lai, W.-C. and Schobert H. H. Ind. Eng. Chem. Res., 1994, 33, 548.

Song, C., Lai, W. -C., Schmitz, A. D., Reddy, K. M., Am. Chem. Soc. Div. Fuel Chem. Prepr., 1996, 41 (1), 71.

Song, C. and Schmitz, A. Am. Chem. Soc. Div. Petrol Chem. Prepr., 1996, 41 (3-4), in press.

Song, C. and Reddy, K. M. Am. Chem. Soc. Div. Petrol Chem. Prepr., 1996, 41 (3-4), in press.

Stanislaus, A. and Cooper, B. H. Catal. Rev. - Sci. Eng., 1994, 36, 75.

Unzelman, G. H. Fuel Reformulation, 1993, May/June, 38.

BENZENE REDUCTION USING OCTGAIN®
- A NEW WAY TO MEET RFG SPECIFICATIONS

P. P. Durand, N. A. Collins, R. Hu, J. C. Trewella and T. L. Hilbert
Mobil Technology Company, PO Box 480, Paulsboro NJ 08066-0480

Keywords: benzene reduction, octane, low sulfur

Introduction

Phase II reformulated gasoline specifications in the U.S. requires refiners to reduce the sulfur, olefins and benzene content of gasoline. Conventional solutions for sulfur reduction such as FCC feed hydrotreating or gasoline hydrofinishing require a large capital investment or lead to a large loss in octane. Mobil's OCTGAIN® process lowers FCC gasoline sulfur and olefin content without a high capital investment and without a loss in octane[1]. This same process can also be used for benzene reduction. Cofeeding a benzene rich reformate fraction to the OCTGAIN process leads to benzene conversions of up to 47%. Depending on the feedstock, there may also be an octane boost of 1.5 numbers for processing heart-cut reformate.

Experimental - feeds

The feedstocks for the study were four different FCC naphthas with different boiling ranges and two heart-cut reformates. The properties are given in Table 1. The octane of the reformates are low despite their high benzene content (39 and 24 wt%) because they also contain significant amounts of low octane n-hexane (24.8 research octane number, 26 motor octane number) and isohexanes (73.4 RON, 73.5 MON). The properties of the different blends were also measured, and these are reported in Table 2.

Experimental - Pilot plant setup

The experiments were conducted in a continuous, fixed-bed pilot plant. Hydrogen flow was once through and liquid feeds were downflow. Pressure was maintained on the system by a high pressure separator with a back-pressure regulator on the gas side and a liquid level control valve. Gases were metered using a wet-test flowmeter, and then sampled by on-line GC. The liquid product was weighed, chilled and sent for octane and composition analysis. All octanes reported in this work are based on full engine tests. Octanes were corrected by subtracting on a volumetric basis the octane of C4- material in the liquid sample, and adding in the contributions of any C5+ material that was found in the offgas. Similarly the C5+ yields are corrected to include any C5+ material in the offgas. Mass closures were typically in the range 97-103 wt%.

Experiments were conducted at typical OCTGAIN process conditions with the OCT-100 catalyst system. The next generation of the catalyst system [2] is expected to show similar benzene reduction performance. Benzene content was measured by GC FTIR or PIONA.

Results - Benzene content

As shown in Figure 1, up to 47% benzene conversion was obtained depending on the feedstock and the temperature of the catalyst system. Benzene is removed by alkylation, but there is also benzene formation by dealkylation of alkylbenzenes. As the temperature of the catalyst system increases, both of these rates increase. When reformate is present benzene alkylation dominates. At sufficiently severe conditions there is also some dehydrogenation of naphthenes, providing an additional route for benzene formation. This is particularly true as pressure is reduced, shifting the equilibrium towards the aromatic species.

The compositional changes that are occurring are shown in Figure 2 as a function of benzene conversion for the two lightest FCC blends. The separation between the curves gives the relative amounts of the different components. As benzene conversion increases, there is initially a reduction in C_7-C_{10} aromatics due to hydrogenation. As severity is increased, aromatics in this boiling range increase due to the desired alkylation of benzene. The technology also gives a dramatic reduction in olefin content. Sulfur removal is not shown in this plot, but is also essentially complete (i.e. > 95 wt%), even at modest benzene conversion levels. At the highest benzene conversion levels there is a yield loss caused by formation of light hydrocarbons, labeled offgas HC in Figure 2. The composition by weight of the light hydrocarbons is typically 2-7% C_1 and C_2, 30-40% C_3, 5-15% mixed C_3 and C_4 olefins, 25-30% iC_4, 25-30% nC_4. Without the presence of reformate, dealkylation of heavy aromatics causes an increase in feed benzene content, the extent of the increase being feed dependent.

The feed benzene content is an important variable affecting overall benzene conversions. The higher the feed benzene content, the higher the conversion. Figure 3 shows the benzene conversion as a function of catalyst temperature for the 215°F+ FCC naphtha feed on its own and in the two blends with reformate. Clearly there is benzene formation for the 215°F+ FCC feed when processed on its own. Note that we have also observed benzene formation in hydroprocessing of FCC gasoline[3]. The feed with 4 wt% benzene shows little benzene

conversion, while there is appreciable conversion for the feed with 6.9 wt% benzene. These results suggest that an equilibrium is established between benzene formation by dealkylation of heavy aromatics and benzene removal, which occurs primarily by alkylation of benzene. Higher feed alkylaromatics will thus be more detrimental to high benzene conversions. This is a function of FCC operation and naphtha end point.

Reducing pressure from 600 to 300 psig causes increased benzene formation by aromatization of cycloparaffins, and so benzene conversion is lower. Consider Table 3 below:

Table 3: Effect of pressure on benzene conversion in OCTGAIN™

Pressure	300 psig	600 psig
C5+ Road Octane	91.2	89.6
Cycloparaffins in product, wt% of total feed	8.9	11.2
Benzene Conversion, wt%	26.1 %	33.1 %

Feed: 215°F+ FCC naphtha, with 2.14:1 v/v FCC naphtha, reformate 2
The same temperature was used for each experiment

The shifts in benzene and other aromatics are driven by thermodynamic equilibrium. Reducing pressure and increasing temperature shifts the hydrogenation / dehydrogenation equilibrium towards aromatics formation. The higher aromatics level at lower pressure also contributes to the improved octane. Note that in each case the product octane is significantly greater than 85.6 which is the feed road octane.

Results - Yield and Octane

By cofeeding reformate, a substantial yield-octane improvement over conventional OCTGAIN was obtained. Figure 4 shows the C5+ yield plotted versus road octane (product - feed). The solid line is the yield versus octane curve for the blend of FCC naphtha and reformate. The yield at 86 octane is slightly above 100% due to a volume expansion over the OCTGAIN catalyst system. A similar yield-octane curve was measured for the FCC naphtha on its own. The dashed line represents what would be achieved if the refiner chose to blend reformate with the OCTGAIN product from processing FCC naphtha on its own. The curve is calculated from volumetrically blending reformate yield and octane (100%, 76.2 road) and FCC naphtha yield and octane (measured in a pilot plant run) in a 1:2 v/v proportion. The data in Figure 4 show a clear improvement when reformate is cofed to the OCTGAIN unit with the FCC naphtha. In particular, at 98 vol% C5+ yield, there is an octane benefit of 1.5 road numbers. We believe that the benefit is due to improved octane uplift for the heart-cut reformate cofeed.

Conclusions/Summary

Benzene conversions as high as 47% were obtained when coprocessing heart-cut reformate with FCC naphthas over the OCTGAIN catalyst system. A road octane benefit of about 1 number at 99 vol% C5+ yield was also observed from cofeeding reformate. This octane benefit may result in an even higher defacto benzene reduction via reoptimization of reformer severity. These results highlight the versatility of the OCTGAIN process in helping refiners meet their RFG needs.

The process with reformate cofeed retains all the other advantages of OCTGAIN. We continue to exploit the unique chemistry of the process, which allows us to have deep desulfurization of the gasoline and a high level of saturation of olefins while retaining a high product octane. This is in contrast to conventional hydrotreating or mild hydrofinishing of FCC gasoline at high LHSV. The economic evaluation of the OCTGAIN process [4] looks attractive, even when the benzene reduction capabilities of the process are not comprehended. With this additional benefit, the technology offers refiners a powerful new tool for manufacture of RFG.

References:

1 Sarli, M. S., Fletcher, D. L., Hilbert, T. L., Karsner, G. G., Shih, S. S. and P. Xayariboun, "OCTGAIN™ A unique Gasoline Desulfurization Process", NPRA 1994 Annual Meeting, March 20-22, 1994

2 Hilbert, T. L., Kirker, G. W., Shih, S., Riedinger, S. L., Timken, H. C., Mazzone, D. N., Holtan, T. P. and M. Schrauben, "OCTGAIN™, A new Desulfurization Process", Hydrofinishing 1 Symposium, AIChE Meeting, March 21 1995, Houston, Texas.

3 Del Rossi, K. J., Riedinger, S. L, and T. L. Hilbert, "Hydrofinishing Olefinic Gasoline", Paper 40C, AIChE Spring National Meeting, Hydroprocessing 1 Symposium, March 21st, 1995

4 Podar, S. K., Chum, K., Ragsdale, R., Hilbert, T. L. and M. S. Sarli, "Octgain™ Evaluation for the Manufacture of Reformulated Gasoline via LP Modeling", National Petroleum Refiners Association (NPRA) 1995 Annual Meeting, Paper AM.95.73, March 19-21, 1995.

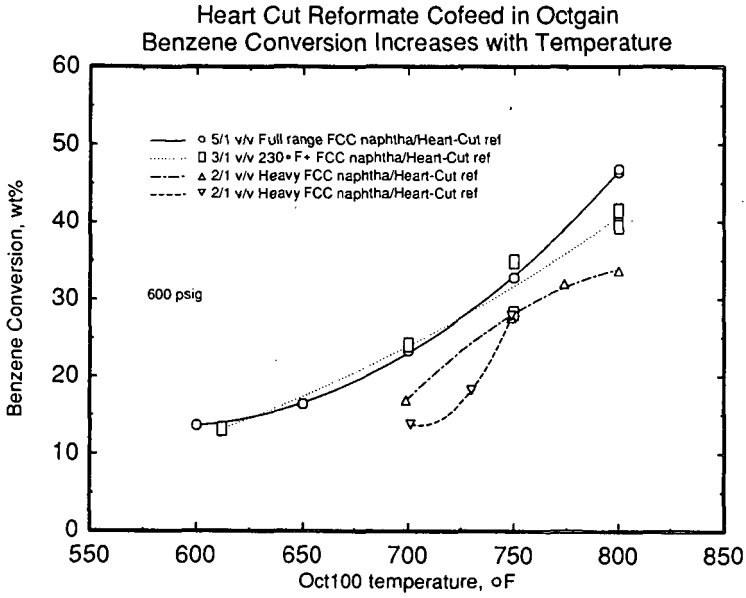
Table 1 : Feed Properties

Feed	Heavy FCC Naphtha	215+ FCC Naphtha	230+ FCC Naphtha	Full-Range FCC naphtha	Reformate 1	Reformate 2
Research Octane	96.4	95.5	93.0	93.3	78.5	74.8
Motor Octane	84.0	83.8	81.5	81.1	73.8	71.8
API	22.8	34.6	41.1	46.3	61.0	67.9
Bromine Number	10.4	17.8	37.1	59.9	5.2	4.9
Sulfur, wt%	1.90	1.00	0.2	0.11		
Nitrogen, ppmw	180	76	98	52		
Distillation (D86), F						
IBP	194	215	232	107		
5 %	382		256	134	150	
10%	394	267	261	146	151	
20%	408		269	165		
40%	427		289	209		
50%	435	319	303	237	157	
60%	443		318	265		
80%	462		352	325		
90%	476	443	373	357	172	
95%	488		387	377	179	
EP	511	491	401	395		
Composition, wt%						
Isopentane					1	0.5
n-Pentane					1.6	1.7
Cyclopentane					1.8	2.4
Benzene	0.1	0.2	0.2	0.9	39.3	24.0
C6 Isoparaffins					28.6	39.9
n-Hexane					14.4	16.6
C6 Naphthenes					1.4	1.3
Toluene					2.3	0.7
C7 Isoparaffins					8.5	9.8
n-Heptane					0.9	1.1
C7 Naphthenes					0.3	0

Table 2: Properties of the blends (Measured, not calculated)

FCC Feed Reformate Feed FCC/Reformate ratio, vol/vol	Heavy Naphtha Ref 1 2/1	230+ Naphtha Ref 1 3/1	Full Range Ref 1 5/1	215+ Naph Ref 2 2.14/1	215+ Naph Ref 2 4.28/1
Research Octane	91.2	90.9	91.9	90.8	93.4
Motor Octane	80.8	80.6	80.5	80.3	81.5
API	32.9	45.7	56.4	43.9	40.0
Bromine Number	12.7	36.3	56.1		
Sulfur, wt%	1.5	0.14	0.11	0.72	0.84
Nitrogen, ppmw	130	71	47	55	64
Distillation (D86), F					
IBP	141	156	106		
5 %	166	190	135		
10%	177	199	143		
20%	197	212	154		
40%	386	253	180		
50%	418	276	197		
60%	425	298	221		
80%	452	338	303		
90%	469	366	345		
95%	494	382	368		
EP	510	398	411		
Benzene, wt%	10.4	9.2	8.3	6.9	4.1

Figure 1



PPD/NAC 3:35pm 5/22/1995 benz_redn

Figure 2

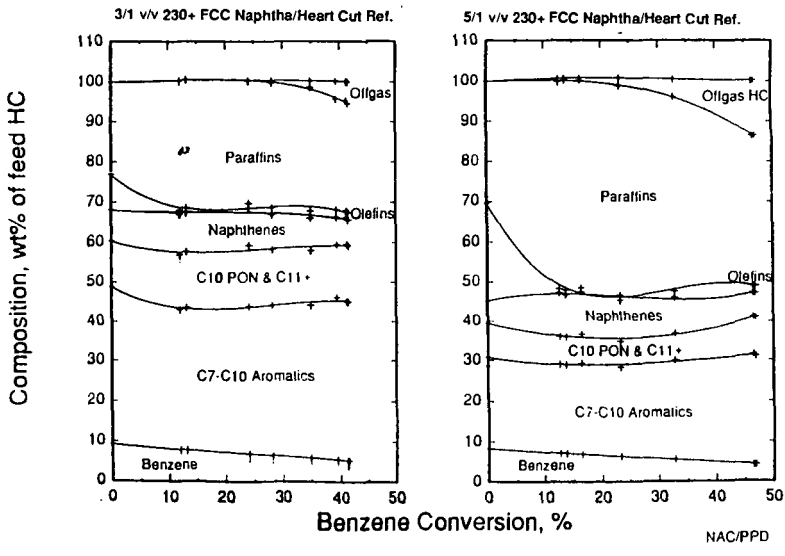
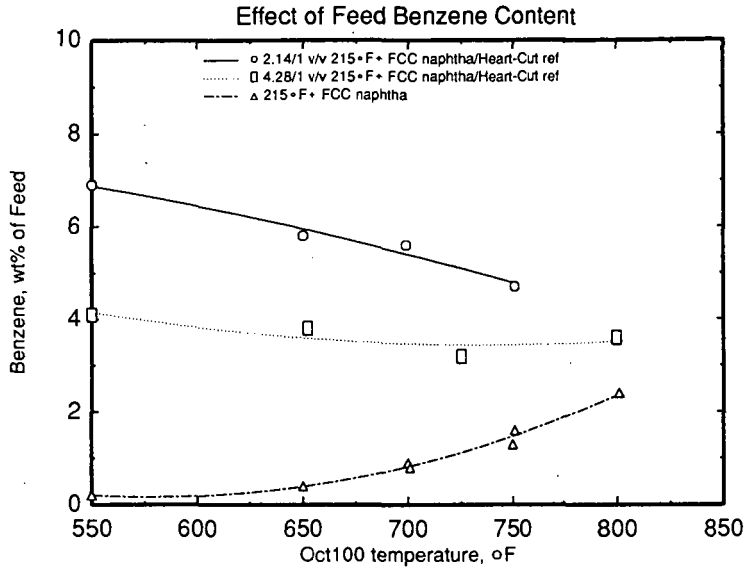
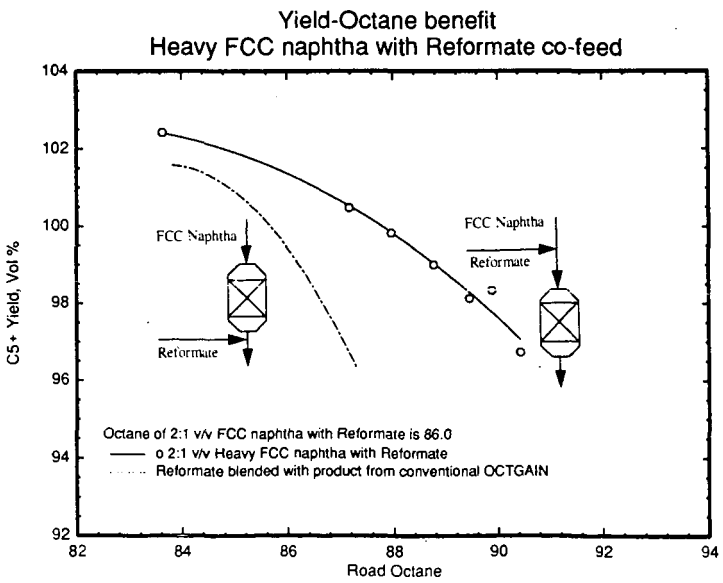


Figure 3



PPD/NAC/RH 3:34pm 5/22/1995 benz_redn

Figure 4



ALKYLATE IS KEY
FOR CLEANER BURNING GASOLINE

J. Randall Peterson
STRATCO, Inc.
4601 College Boulevard, Suite 300
Leawood, KS 66211

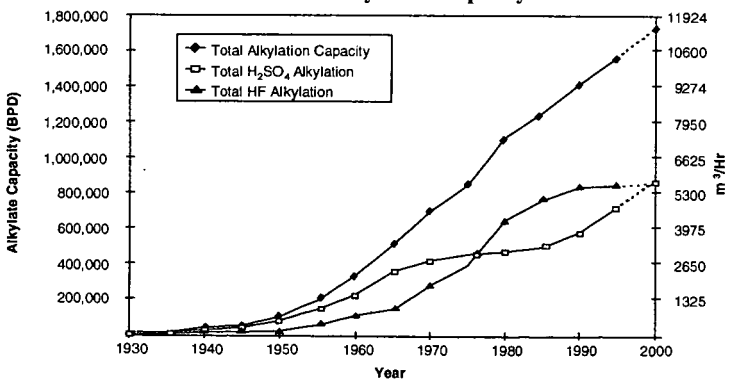
KEYWORDS: STRATCO, ALKYLATION, RFG

ABSTRACT
Alkylate is a key component in cleaner burning gasoline. The alkylation process reacts light olefins (propylene, butylenes, and amylenes) with isobutane in the presence of a strong acid catalyst. The alkylate that is produced consists of branched paraffins having a low Reid vapor pressure (Rvp), high research and motor octane numbers (RON & MON), low sulfur content, and a good driveability index (DI). Therefore, alkylation removes olefinic, high Rvp components from the gasoline pool and converts them to an ideal, high octane blendstock for cleaner burning gasoline.

INTRODUCTION
The intent of cleaner burning or "reformulated" gasoline is to reduce ground-level ozone formation by reducing the amount of volatile organic compounds (VOCs) emitted from automobiles during the high ozone season (primarily summer). Reformulated gasoline also strives to reduce toxic air pollutants throughout the year. These toxics include benzene, polycyclic aromatics, butadiene, formaldehyde, and acetaldehyde. The primary emission precursors are thought to be high Rvp gasoline components along with olefins, benzene, aromatics, and sulfur.

Alkylate from a modern STRATCO Alkylation Unit adds zero or negligible amounts of these emission precursors and toxics and reduces the Rvp of the gasoline pool. In addition, alkylate lowers the levels of benzene, aromatics, and sulfur through dilution and helps replace some of the octane lost when lead or aromatics are taken out of gasoline. For these reasons, an increase in the demand for alkylate is seen due to the increased worldwide requirements for cleaner burning gasoline.

Figure 1
Worldwide Alkylation Capacity



Source: Oil and Gas Journal, 1938-1994

In the United States, government legislation in the form of the 1990 Clean Air Act Amendments attempts to address the issue of excessive levels of ground-level ozone in the more populated areas of the country. As recently as 1987, approximately 100 metropolitan areas in the U.S. failed to meet the mandated ground-level ozone standard of 120 ppb. Ozone is of concern because even in very low concentrations it can cause damage to the lungs. It forms in the lower atmosphere as a result of reactions between hydrocarbons, nitrous oxides and sunlight.

Copyright 1996 STRATCO, Inc.

Many other countries have watched the United States enact this legislation and are considering similar requirements. It is hoped that by producing cleaner burning gasoline, that some of the air quality problems surrounding the larger cities may be alleviated. While many countries are moving toward cleaner burning gasolines, no one other than the United States has passed a piece of legislation with the broad coverage of the Clean Air Act.

TRENDS

Legislation that requires reduced Rvp and benzene drives refiners to include more alkylate and ethers in the gasoline pool. In the U.S., alkylate is already being used as much for Rvp control as for octane. This trend will only increase in coming years. Significant increases in alkylate capacity may be required, especially with the larger emissions reductions of 29% in VOCs, 22% in toxics, plus a 6.8% reduction in NO_x required in the year 2000.

In California, the low olefin and Rvp specifications are driving several refiners to alkylate their amylenes. This has required an increase in their alkylation unit capacities. Furthermore, some refiners are considering changes in FCC catalyst to increase the amount of light olefins available for use as feedstock to the alkylation and etherification units.

Properties of alkylate that are exceptionally attractive to refiners are shown in Table 1. For comparison purposes, other common blending components are shown as well.

Table 1
Gasoline Blendstocks and Their Typical Properties

	Alkylate	FCC Naphtha	Reformate	Poly Gasoline
Aromatics, LV%	0	29	63	0
Olefins, LV%	0	29	1	95
Sulfur, ppmw	26*	756	55	125
T_{50}, °F (°C)	216 (102)	220 (104)	256 (124)	236 (113)
T_{90}, °F (°C)	289 (143)	366 (186)	334 (168)	346 (174)
Driveability Index**	1134	1223	1299	1251
RON	93.2	92.1	97.7	94.4
MON	91.I	80.7	87.4	81.9

Source: NPRA Survey of U.S. Gasoline Quality, January 1991

* Alkylate sulfur values of less than 10 ppmw are typically reported for STRATCO Units.

** $DI=(1.5 \times T_{10}) + (3.0 \times T_{50}) + T_{90}$ (D86 T values are in °F). Since the T_{10} value is highly dependent on the Rvp of the finished gasoline product, a value of 131°F (55°C) was assumed for all blendstocks.

As Table 1 shows, alkylate is an ideal blendstock. It has negligible amounts of toxics and ozone precursors. It has high RON and MON values. And its DI is consistently below the limit of 1200 currently proposed by the American Automobile Manufacturers Association (AAMA).

ALKYLATION CATALYSTS

Alkylation catalyst options for refiners today consist of hydrofluoric (HF) and sulfuric (H_2SO_4) acids. H_2SO_4 represents 45% of the world's installed capacity and HF represents 55%.

There is a significant amount of research being conducted on alternate alkylation catalyst technologies, primarily solid catalysts, but as of this date there are no commercially proven processes. Additional information on each of the research efforts in this area is supplied at the end of this paper.

STRATCO has been instrumental in developing options for refiners with HF alkylation units to convert to H_2SO_4 catalyst. STRATCO's ConvEx™ low cost HF to H_2SO_4 Conversion/Expansion Revamp Process reuses both the reaction and distillation sections of the existing HF alkylation unit. Both Phillips and UOP-designed HF alkylation units can be converted to H_2SO_4 alkylation units for about the same cost as installing mitigation facilities ($20 - 30 million U.S.). This revamp eliminates the safety hazards associated with HF, typically allows for a significant capacity increase, and often improves the octane of the alkylate product.

Feed Availability and Product Requirements

Historically, butylenes from the FCC were the traditional olefins fed to the alkylation unit. Today, alkylation units are using a broader range of light olefins including propylene, butylenes and amylenes. Alkylate composition and octane from pure olefins and mixed olefins are quite different for each catalyst as shown in Table 2:

Table 2
Alkylate Octanes

	H_2SO_4		HF	
	RON	MON	RON	MON
Propylene	89-92	88-90	91-93	89-91
Butene-1	97-98	93-94	90-91	88-89
Butene-2	97-98	93-94	96-97	92-93
Isobutene	90-91	88-89	94-95	91-92
Amylenes	90-92	88-90	90-92	88-89

Propylene

Alkylation of propylene in an HF unit is advantageous due to a significant hydrogen transfer side reaction that occurs:

Primary Alkylation in HF: $C_3^= + iC_4 \rightarrow C_7$ Alkylate

Hydrogen Transfer Reaction: $C_3^= + 2iC_4 \rightarrow C_3 + C_8$ Alkylate

This reaction will cause an increase in alkylate octane resulting from equimolar production of more C_8 alkylate (from the $iC_4^=$ formed) and less C_7 alkylate (since $C_3^=$ has disappeared). Reaction extent varies greatly, with 15-20% being common, while the reaction is favored by process conditions (such as high isobutane/olefin ratios) which produce high quality alkylate. Refiners must carefully analyze isobutane and propane price projections and the value of incremental octane to determine the impact of this reaction on unit economics.

Butylenes

Composition and quality of alkylates produced from butene-1 and butene-2 are very similar for H_2SO_4 alkylate but not for HF alkylate. When butene-1 is used, HF alkylate contains a lower amount of trimethylpentanes (TMP's) and a greater amount of dimethylhexanes (DMH's) than H_2SO_4 alkylate. This composition difference results in a several octane number advantage for H_2SO_4 alkylate. Conversely, alkylate produced from butene-2 is similar whether produced from the H_2SO_4 or HF process. Although not shown, distribution of TMP's varies significantly, with HF alkylates having a higher concentration of 2,2,4-TMP (100.0 RON) but a lower concentration of the other TMP isomers.

The 2,3,3- and 2,3,4-TMP's (109.6 and 106.1 RON, respectively) are more predominant in H_2SO_4 alkylate, accounting for the slight octane advantage. HF alkylation with isobutene yields a product that has a higher concentration of TMP's resulting in a several octane number advantage over the corresponding H_2SO_4 alkylate. Addition of an MTBE unit ahead of an alkylation unit improves H_2SO_4 alkylate quality and reduces HF alkylate quality.

Amylenes

Amylenes have traditionally been left in the FCC gasoline pool due to their relatively high octanes. However, these constituents also have high Rvp values. As refiners continue to look for means of reducing the Rvp of the gasoline pool, STRATCO is seeing continued interest in alkylation of these components. For comparison purposes, the octanes and Rvp of amylene alkylate are also provided in Table 3.

Table 3
C_5 Octanes and Vapor Pressures

	RONc	MONc	Rvp (Psi / Bar)
1-Pentene	90.9	77.1	19.1 / 1.32
2-Pentene*	~94	~80	15.3 / 1.06
2-Methyl-1-Butene**	102.5	81.9	18.4 / 1.27
2-Methyl-2-Butene	97.3	84.7	14.3 / 0.99
3-Methyl-1-Butene***	?	?	26.4 / 1.82
Cyclopentene	93.3	69.7	? / ?
Isopentane	92.3	90.3	20.4 / 1.41
Pentane	61.7	62.6	15.6 / 1.08
C_5 Alkylate	**91.5**	**90.0**	**3.0 / 0.21**

* 2-Pentene octane values not found in literature. Values are estimated.

** Literature specifies 2-Methyl-1-Butene RONc equal to 0.2 gm of lead per gallon of 2,2,4-trimethylpentane. 102.5 value is estimated.

*** 3-Methyl-1-Butene octane values are not found in literature.

Amylene alkylate octanes from either a H_2SO_4 or HF alkylation unit have lower octanes than those produced with other feedstocks. In H_2SO_4 alkylation of amylenes, acid consumption increases about 30 to 50% above that for butenes. In an HF unit, acid soluble oil production increases when amylenes are alkylated.

Safety & Environmental Considerations

Safety and environmental concerns are extremely important when choosing an alkylation technology. A huge concern is the large volume of LPG present within the unit. Refineries must protect against conditions that could lead to LPG releases and potential fire hazards. All of the alkylation technologies being evaluated have similar volumes of hydrocarbon within the unit. In addition, neither acid catalyst impacts the flammability of LPG, therefore, no one technology has an advantage over another in this regard.

Another major safety concern is the acid catalyst used to promote the reaction. Both HF and H_2SO_4 acids are hazardous materials, however, HF is considerably more dangerous. In the United States, HF has been identified as a hazardous air pollutant in current federal and state legislation. Sulfuric acid has not.

HF and H_2SO_4 represent a potential danger to personnel working on alkylation units. Contact with either HF or H_2SO_4 can result in chemical burns. However, HF burns tend to be more severe since the fluoride ion penetrates the skin and destroys deeper layers of tissue. If not treated, it may even cause dissolution of the bone. In addition, inhalation of HF vapors may cause pulmonary edema and, in severe cases, may result in death.

The volatility of the acid at ambient conditions is a chief concern. HF is a toxic, volatile gas at these conditions while H_2SO_4 is a toxic liquid. Therefore, H_2SO_4 is much easier to contain in the event of an accidental release. In more densely populated areas of the world, safety and environmental concerns of HF usage have given H_2SO_4 alkylation a notable advantage.

In 1986, tests were conducted in the Nevada desert to determine the dangers of a possible HF liquid release. Under conditions similar to those that exist in an alkylation unit, lethal concentrations of an HF aerosol were present up to 5 miles from the release points. During these tests, HF releases were observed to be much more dangerous than previously thought.

Although HF alkylation plants have, for many years, had good safety records, several accidents that have occurred in the past ten years have raised questions about potential dangers. The most serious accident occurred in October, 1987, in Texas City, Texas. A piece of equipment was dropped on an overhead line from a partially filled HF tank. The line ruptured and allowed HF to vaporize and form a toxic aerosol cloud. As a result, 3,000 people were evacuated from the nearby community and several hundred people were hospitalized. Another accidental release of HF at a different refinery in the late 1980s killed one refinery worker and critically injured another. An incident in the early 1990s killed two pump maintenance workers.

Due to these risks, many refiners are implementing water mitigation and detection devices in an effort to remove any HF that would vaporize in the event of a release. With water/HF ratios of 40:1, nearly 90% of the HF can be removed. However, these systems are expensive and there is the concern that the water sprays could become inoperative as a result of an accident. In addition, details have not yet been obtained, or at least reported, on the fate of the HF that is not removed by the water sprays. Many refiners with HF units are also considering HF modifiers to reduce the vapor pressure and thus the aerosol-forming tendencies of HF. These HF modifiers are still in the development stage and are expected to be used in combination with mitigation systems. Recent tests of two of these additives have indicated substantial reductions in HF aerosol and vapor cloud formation. Figures quoted are in the range of 63-80% reduction of airborne HF due to the additive. When coupled with an effective mitigation system, reduction in the quantity of airborne HF would be in the range of 95-97% compared to an unmitigated release from an alkylation unit without additive.

Tests conducted in 1991 by Quest Consultants, Inc. showed that the potential for a H_2SO_4 aerosol formation from an alkylation unit release is highly unlikely. Several tests were performed under a variety of conditions resembling those observed in an alkylation unit. The tests provided conditions favorable to the formation of airborne particles. However, the released acid did not remain airborne and an aerosol was not formed. It is apparent, based on these tests, that a sulfuric acid aerosol will not form under conditions similar to those present in a STRATCO Effluent Refrigerated Alkylation Unit.

SOLID CATALYST DEVELOPMENTS

Research in the area of a solid catalyst for alkylation has been ongoing for many years. Numerous patents exist for different catalysts, catalyst supports, and processes. It is well known that Lewis acids will catalyze the alkylation reaction (alkylation of isobutane with olefins was discovered using aluminum chloride promoted with HCl). Several of the current preferred solid catalysts use a salt of HF: either boron trifluoride (BF_3) or antimony pentafluoride (SbF_5). Since every alkylation process produces heavy polymers, solid catalysts have the tendency to foul quickly. Therefore, the solid catalyst process has two major hurdles to overcome: catalyst life and catalyst regeneration. Several companies are engaged in active research in this area, but no one has yet commercialized a new alkylation technology.

Catalytica

A joint venture of Neste Oy, Conoco, and Catalytica started up a 7 BPD (0.05 m^3/hr) pilot plant in January, 1993 at Neste's Technology Center adjacent to their refinery in Porvoo, Finland. It has been operating on MTBE raffinate. According to the patent literature, the research group is testing boron trifluoride on an alumina support.

The technology requires a feed preparation section to reduce water and impurities such as sulfur and oxygenates. A CSTR reactor configuration using a dilute slurry of catalyst is currently being used although other reactor designs are being considered. Catalyst is continually removed from the reactor and continually regenerated. Spent catalyst exits the regeneration section and is disposed as non-hazardous waste. With MTBE raffinate, the research group reports that they have been able to produce good quality alkylate with high octane at reasonable I/O ratios (5-12).

However, it has been stated that additional funding for the project from Neste Oy and Conoco has been discontinued. As a result, the pilot plant is no longer operational. It appears that these partners feel that this process does not have a significant economic advantage over the existing alkylation technologies. Catalytica continues to promote the technology, although they will need an additional funding source to continue their research, development and commercialization efforts.

Haldor Topsoe

Haldor Topsoe's technology utilizes triflic (trifluoromethanesulfonic acid) on a bed of silica. The triflic is supported on the silica in a plug flow, packed bed reactor. Haldor Topsoe claims that since their technology is not a true solid catalyst but rather a liquid catalyst on a solid support, that less deactivation of the catalyst occurs. They have been operating a 0.5 BPD (0.003 m^3/hr) pilot plant since 1991.

With time, the triflic migrates from one end of the bed to the other. As the acid catalyst breaks through, it is sent to an acid recovery unit for separation of ASO and acid. An alkylate wash unit is used to remove the catalyst from the alkylate product. The reaction's optimal temperature has not been made clear; they have stated that this technology may or may not require refrigeration. However, if octane is valuable, refrigeration is recommended. Haldor Topsoe is working with the M.W. Kellogg Company on the engineering for this process. They are currently looking for a refining partner to participate in scaling up this technology.

IFP

IFP has done some work with a fluorine modified zeolite, but they report that the prospects for zeolites in alkylation are not good due to poor selectivity and stability. Recent work appears to be centered around "promoted H_2SO_4" on silica. Not much information has been released about their research.

Kerr McGee

Kerr McGee has done some preliminary, laboratory scale work using aluminum chloride at levels of less than 1% as a promoter for the alkylation reaction. With this scheme, the catalyst is actually soluble in the hydrocarbon phase. As the catalyst ages, it will precipitate out of the hydrocarbon and then can be gravity separated for recovery and regeneration.

In order to proceed in the research and development of this technology, Kerr McGee will require a partner for funding. The Kerr McGee Corporation is currently engaged in exiting from the refining business.

Mobil

Mobil has been granted many patents on solid catalysts for alkylation. Most of these involve boron trifluoride plus zeolites as the catalyst.

CR&L

CR&L (a partner with ABB Lummus in the CD Tech joint venture) is doing research with a salt of antimony pentafluoride on a silica support. Their scheme uses a fluidized bed at a relatively cold temperature, similar to that of the H_2SO_4 alkylation process. The 10 BPSD (0.07 m^3/hr) pilot plant that they were operating at Clark's Port Arthur, TX refinery since December of 1993, was shut down in 1995. The company cited wide feedstock fluctuations and their negative impact on the catalyst as the primary reason for shutting down the pilot plant. CR&L has subsequently been operating a bench scale pilot plant at their office in Pasadena, TX with a capacity of 1 BPSD (0.01 m^3/hr). They are refocusing their efforts in an attempt to improve catalyst regeneration requirements.

UOP

UOP is also working on solid catalyst alkylation technology, referred to as SCA, although little technical data is available on the process. They have been granted patents utilizing carbon supported HF and zeolites. We believe that in order to minimize catalyst regeneration, a rather extensive feed pretreatment system would be required to reduce feed contaminants down to very low levels.

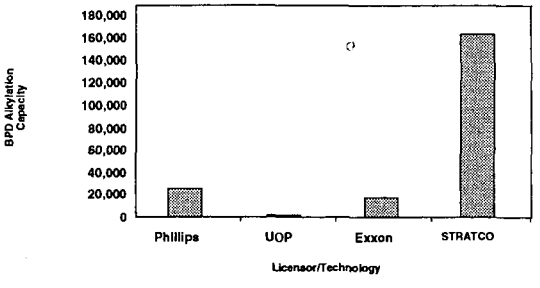
Very few details are available on the specifics of the reactor employed by UOP for this process. Olefin conversion is said to be nearly 100% depending upon the frequency of internal catalyst regeneration. UOP claims the alkylate product is comparable to that produced in either an H_2SO_4 or HF alkylation unit. We understand that this comparison has only been made for one particular butylene isomer and the same comparison has not been made for a standard refinery alkylation feed.

From a utility and capital standpoint, UOP has stated that they expect SCA expenses to be somewhat higher than existing HF technology expenses and to be comparable with existing H_2SO_4 technologies. Until this technology is used commercially, these claims cannot be challenged.

SUMMARY

International demand for alkylation technology will continue to increase as countries look to their refining industries to produce cleaner burning fuels. Due to heightened concerns over the safety of HF, the majority of alkylation technology implemented in the last five years has been H_2SO_4 technology. During this time, over 90% of the H_2SO_4 alkylation unit revamps & expansions as well as grassroots units built throughout the world have been designed by STRATCO (shown in Figure 2).

Figure 2
Installed Alkylation Capacity (1990-1995)



While the search for a commercially proven solid catalyst technology continues, STRATCO is committed to finding ways to improve our technology as well. We currently have an extensive alkylation R&D program underway with a goal of minimizing catalyst requirements and improving equipment efficiencies for our technology. We are also committed to providing cost-effective methods to convert HF alkylation units to use H_2SO_4 catalyst. For about the same cost as mitigation, STRATCO's ConvEx™ conversion revamp eliminates the liability of HF permanently, typically allows for a significant capacity increase, and usually improves the octane of the alkylate product.

STRATCO will continue in our efforts to provide the utmost in customer service and maintain our position as the leading licensor of alkylation technology well into the 21st century.

PREPRINT EXTENDED ABSTRACT
Presented Before The Division Of Environmental Chemistry
American Chemical Society
Orlando, FD August 18-23, 1996

The Analysis of Reformulated Gasolines Using Fast Gas Chromatography / Mass Spectrometry

Vincent P. Nero and Donald E. Drinkwater,
Texaco FLTD, Beacon, NY 12508

The requirement that all reformulated gasoline (RFG) sold in the United States be analyzed by gas chromatography / mass spectrometry (GC/MS) for aromatic content presents a unique challenge and opportunity for petroleum analytical analyses. A fast GC/MS method was developed which encompasses or surpasses not only the basic EPA performance requirements for analysis of total aromatics, but will simultaneously measure individual aromatics and oxygenates in reformulated gasolines. Furthermore, the combined procedure requires only 10 minutes of instrument and computational time. In contrast, ASTM Method D 5769 generally takes 90 minutes just to measure total aromatic content. The measurements of oxygenates, benzene, and toluene also compare favorably to the standard ASTM methods. The method matches the precision and accuracy of ASTM Method D3606, a GC/GC method, which is the only current acceptable method for individual aromatics in RFG. Furthermore, it can measure methyl *t*-butyl ether (MTBE) and *t*-amyl methyl ether (TAME) as accurately as ASTM D5599, the approved OFID method for oxygenates.

The fast chromatography method meets of all of the requirements of the EPA and ASTM methods. The EPA primarily list performance objectives requiring GC/MS and 2% overall accuracy. The ASTM Method does not restrict the chromatography or types of internal standards. The Texaco Method has procedural enhancements which enable it to expand the basic scope of these methods beyond total aromatics and to surpass their precision and accuracy while maintaining performance requirements of both the EPA and ASTM methods. These enhancements are:

- The additional use of deuterated surrogate, toluene, which is not required, but allowed by the ASTM method.
- The use of micro-bore capillary gas chromatography, which reduces greatly processing time, and prevents ion saturation of the mass spectrometer source.
- More appropriate selection of quantitation ions, which enhances precision and accuracy without changing any operating procedures.

Since toluene is generally the most abundant individual aromatic hydrocarbon component in gasoline, its accurate measurement is critical. (The EPA requires that total aromatics in RFG be measured to the within 2% of the theoretical value.) Benzene is a poor choice as an internal standard for toluene for two reasons. First, benzene is found in commercial gasolines at a much lower level than toluene. (~0.1-.5% vs. ~10%) Second, benzene has a very different mass spectral fragmentation pathway. It lacks a benzylic carbon-carbon bond. The addition of a deuterated toluene surrogate at an appropriate concentration ensures its accurate measurement.

Typical calibration curves illustrating benzene and toluene are shown in *Figures 1 and 2.* Both curves are essentially linear over the entire concentration range with correlation coefficients approaching 1.0.

The use of micro-bore and mini-bore capillary GC columns for quantitative analysis provides a number of advantages over conventional capillary columns. In addition to the decreased elution time provided by the more efficient separation, the decreased capacity of these columns may be used to increase the dynamic range of the mass spectrometer, thus improving calibration linearity and accuracy. The smaller inside surface area and shorter length of these columns leads to a much reduced phase bleed level in the ion source, lengthening the time between ion source cleanings and, therefore, instrument recalibration. The decreased gas flow through the narrow-bore columns greatly improves the gas load into the ion source, as well as simplifying the running of these columns at high split ratios for neat samples such as gasolines.

Figure 3 shows the comparison of the chromatography using a conventional capillary column and a micro-bore capillary column in the region of C_3-benzenes (trimethyl benzenes, ethyl methyl benzenes, and propyl benzenes). Note that there is no loss of chromatographic resolution or change in the relative ion abundances, but the GC retention time has been reduced from 38 minutes to 6 minutes.

Ten full mass range scans across each GC peak are necessary for adequate precision. The mass spectrometry should be capable of scanning from 45 to 250 amu every 0.1 seconds. Most modern commercial instruments can achieve this rate. The Texaco method has been implemented on four different mass spectrometers from three different vendors.

Table 1 shows typical repeatability for this method (generally the standard deviations are less than 0.5). The EPA requires accuracy within 2.0% of the actual value. *Figure 4* shows a comparison of benzene data using this method, which was collected on four different GC/MS systems.

Comparison to other standard methods.

Figure 4 also compares the analysis of benzene in gasoline using ASTM Method D3606 (a GC/GC column switching method, which is the only current acceptable method for individual aromatics in RFG) and the Texaco GC/MS Method. The results of both methods is essentially identical. (However, the Texaco Method also simultaneously measured all the individual aromatics, their total sum, and oxygenates.)

Table 2 compares the analysis of total aromatics in gasoline using the Texaco fast GC/MS method with the ASTM Method D1319, using fluorescent indicator adsorption open column liquid chromatography (FIA), ASTM Method D5769 (the routine total aromatic method using GC/MS), and ASTM D5580 Method (a GC/GC column switching method being adopted by CARB). The FIA method is not precise, but it is on average accurate. The average of 65 different laboratories produced results essentially the same as the Texaco fast GC/MS Method. The routine ASTM D5780 generally will result in somewhat lower total aromatics, since the method does not currently consider the differences in mass spectral response factors between carbon and hydrogen benzylic losses in the heavier alkyl aromatic region. For example pentamethyl benzene molecular ion has a very different relative response factor to that of the pentyl benzene.

Figure 5 compares the analysis of MTBE and TAME using the fast GC/MS method and the ASTM Method D5599 (OFID). Again, the Texaco Method results are essentially the same as the OFID results. Again, it must be noted that these results were obtained simultaneously with the measurements of benzene, toluene, and total aromatics.

figure 1

Benzene Calibration

Benzene m/z 78 (0.1 to 5 wt%) vs. Benzene-d6 m/z 83,84 (2 wt%)

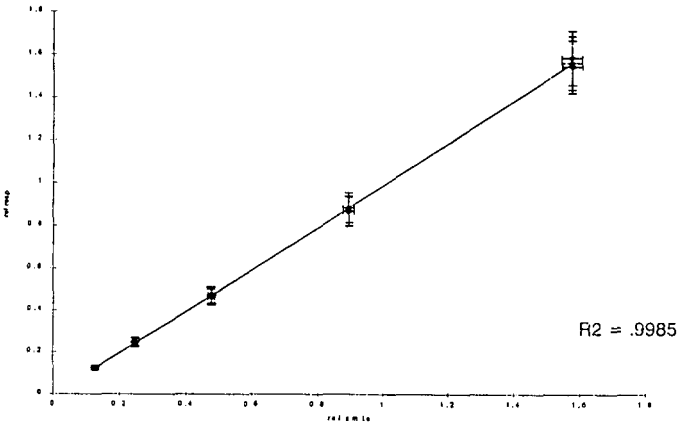
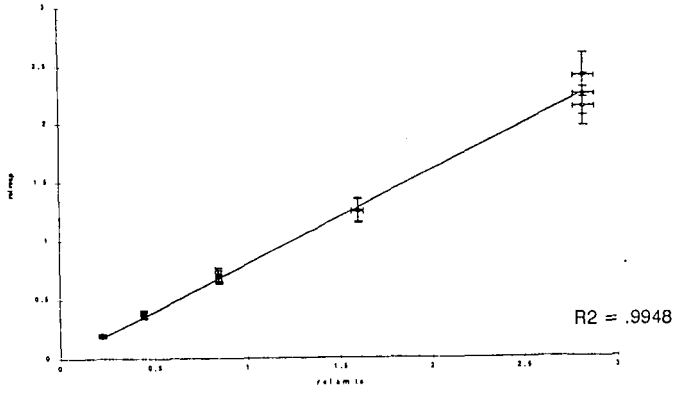


figure 2

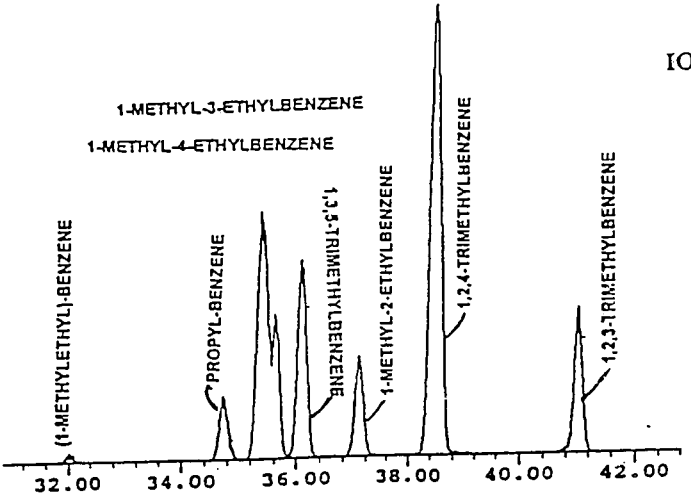
Toluene Calibration

Toluene m/z 92 (2 to 20 wt%) vs. Toluene-d8 m/z 99,100 (7 wt%)



Generally used version of ASTM Method
SIR Chromatogram

figure



Texaco Version SIR Chromatogram
(still meets all EPA and ASTM requirements)

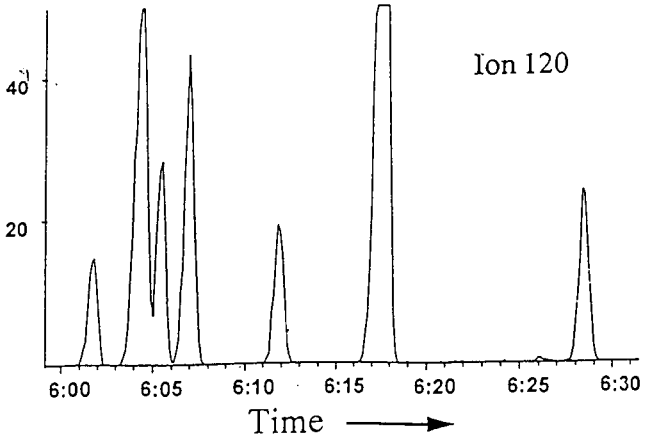


figure 4

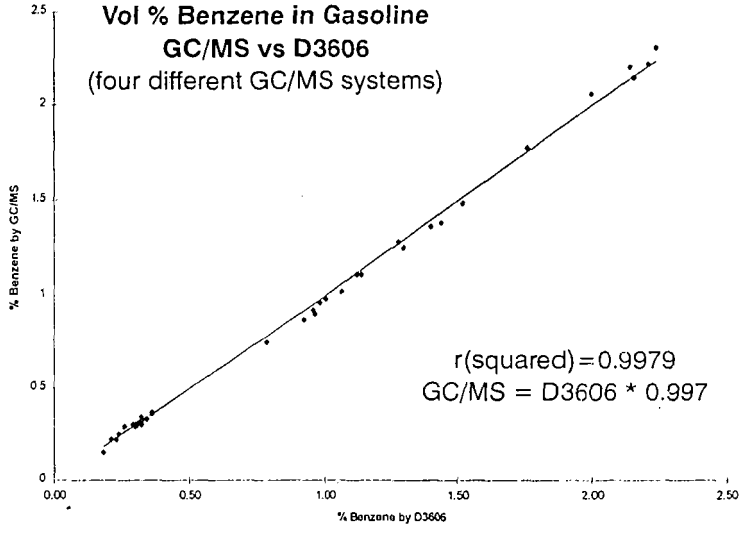
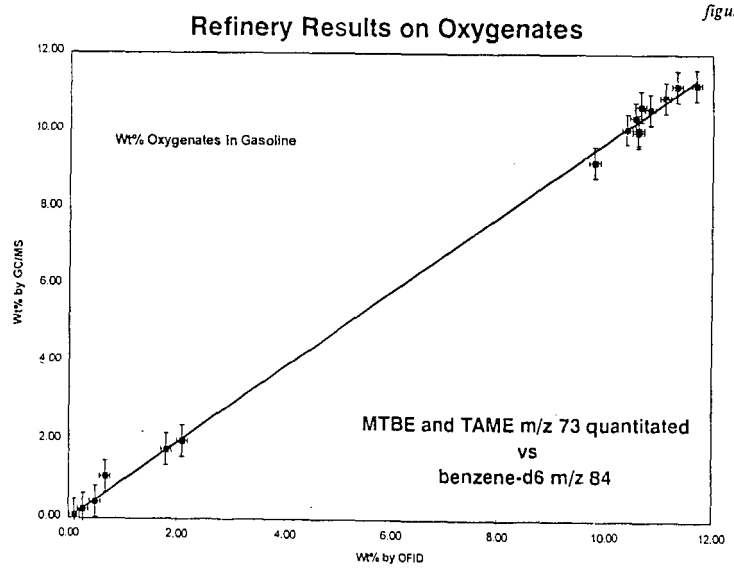


figure 5



Sample Precision (wt %)

table 1

Compound	#1	#2	#3	#4	Average	Std Dev
Benzene	**1.13**	**1.16**	**1.20**	**1.15**	**1.16**	**0.03**
Toluene	8.80	8.45	8.66	8.28	8.55	0.23
ethyl benzene	2.30	2.30	2.34	2.18	2.28	0.07
m,p xylene	5.04	5.09	5.23	5.04	5.10	0.09
o-xylene	1.73	1.71	1.77	1.64	1.71	0.05
cumene	0.07	0.09	0.08	0.07	0.08	0.01
propyl benzene	0.36	0.39	0.36	0.37	0.37	0.01
m-ethyl toluene	1.15	1.18	1.20	1.20	1.18	0.02
p-ethyl toluene	0.70	0.72	0.68	0.70	0.70	0.02
1,3,5-trimethyl benzene	0.59	0.60	0.59	0.58	0.59	0.01
o-ethyl toluene	0.38	0.36	0.36	0.38	0.37	0.01
1,2,4-trimethyl benzene	1.73	1.72	1.71	1.73	1.72	0.01
1,2,3-trimethyl benzene	0.32	0.33	0.34	0.32	0.33	0.01
indan	0.55	0.56	0.55	0.59	0.56	0.02
C4 benzenes (cymenes)	0.11	0.08	0.11	0.12	0.10	0.01
C4 benzenes (straight chain)	1.49	1.46	1.50	1.47	1.48	0.02
C4 benzenes (tetramethyl)	0.29	0.29	0.27	0.26	0.28	0.01
C6 benzenes	0.08	0.09	0.08	0.08	0.08	0.01
naphthalene	0.19	0.20	0.20	0.20	0.20	0.01
C5 benzenes	0.22	0.22	0.20	0.22	0.21	0.01
2-methyl naphthalene	0.18	0.18	0.18	0.18	0.18	0.00
1-methyl naphthalene	0.07	0.08	0.08	0.06	0.07	0.01
TAME	0.0	0.0	0.0	0.0	0.0	0.0
MTBE	11.5	11.2	11.5	11.4	11.4	0.1
Total Aromatics	**27.46**	**27.25**	**27.69**	**26.82**	**27.30**	**0.37**

table 2

	Jul-95			
Aromatics			2SD	N
ASTM FIA (Corrected)	25.46	+/-	3.76	65
Texaco fast GC/MS	25.60			
routine ASTM D5769 GC/MS	20.94	+/-	2.00	27
ASTM 5580	27.20	+/-		2
Benzene				
ASTM 3606	0.63	+/-	0.12	50
Texaco fast GC/MS	0.65			
routine ASTM D5769 GC/MS	0.63	+/-	0.10	20
ASTM 5580	0.59			2

	Aug-95			
Aromatics			2SD	N
ASTM FIA (Corrected)	21.09	+/-	4.06	49
Texaco fast GC/MS	19.32			
routine ASTM D5769 GC/MS	17.47	+/-	3.12	33
ASTM 5580	19.73	+/-	1.96	3
Benzene				
ASTM 3606	0.29	+/-	0.04	56
Texaco fast GC/MS	0.29			
routine ASTM D5769 GC/MS	0.30	+/-	0.02	25
ASTM 5580	0.26	+/-	0.02	3

	Sep-95			
Aromatics			2SD	N
ASTM FIA (Corrected)	13.59	+/-	2.08	54
Texaco fast GC/MS	13.88			
routine ASTM D5769 GC/MS	12.79	+/-	1.58	34
ASTM 5580	14.41	+/-	2.14	3
Benzene				
ASTM 3606	0.26	+/-	0.08	58
Texaco fast GC/MS	0.27			
routine ASTM D5769 GC/MS	0.28	+/-	0.06	28
ASTM 5580	0.23			2